RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXIV NUMBER 2

April-June, 1951

Published Quarterly under the Auspices of the
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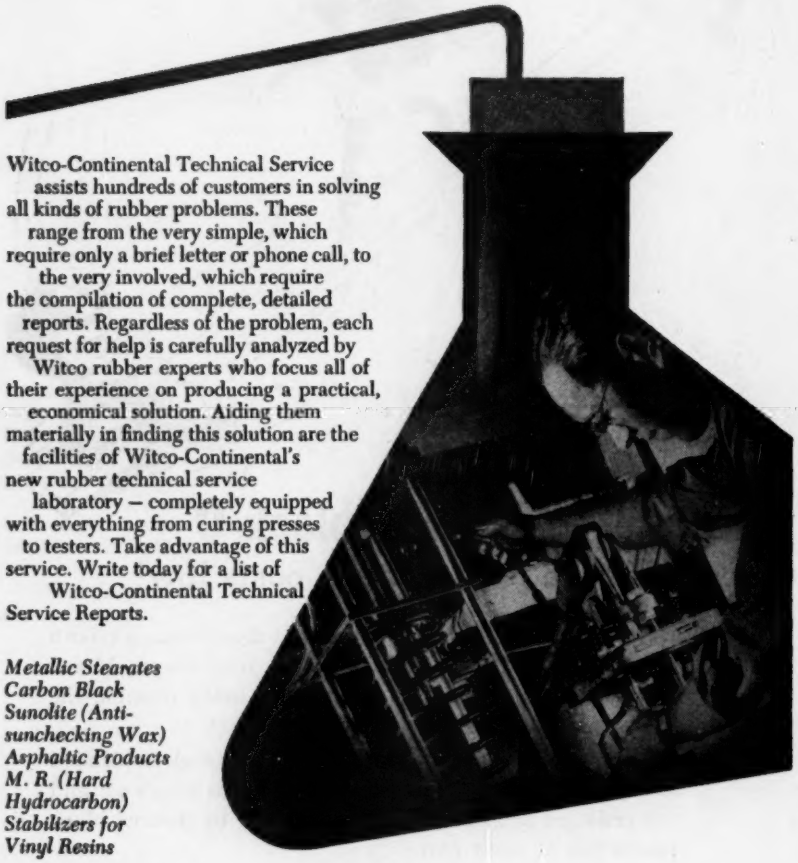

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Chairman....P. J. SICK (Hewitt-Robins, Inc., Buffalo). *Vice-Chairman*....F. A. KOHLHAGEN (Globe Woven Belting Co., Buffalo). *Secretary-Treasurer*....R. J. LOWRY (Hewitt-Robins, Inc., Buffalo). (Terms expire December 31, 1951.)

CHICAGO

Chairman....P. F. NIESSEN (Victor Manufacturing & Gasket Co., Chicago). *Vice-Chairman*....J. F. TAYLOR (Commercial Solvents Corp., Chicago). *Secretary-Treasurer*....J. E. A. HOPKINS (Van Cleef Brothers, Chicago). (Terms expire April 20, 1951.)

CONNECTICUT

Chairman....C. A. LARSON (Whitney Blake Co., Hamden, Conn.). *Vice-Chairman*....G. R. SPRAGUE (Sponge Rubber Products Co., Derby, Conn.). *Secretary*....G. A. DI NORSCIA (Sponge Rubber Products Co., Derby, Conn.). *Treasurer*....F. J. ROONEY (General Electric Co., Bridgeport, Conn.). (Terms expire December 31, 1951.)

DETROIT

Chairman....G. F. LINDNER (Minnesota Mining & Manufacturing Co., Detroit). *Vice-Chairman*....G. R. CUTHBERTSON (U. S. Rubber Co., Detroit). *Secretary*....G. P. HOLLINGSWORTH (Minnesota Mining & Manufacturing Co., Detroit). *Treasurer*....E. V. HINDLE (U. S. Rubber Co., Detroit). (Terms expire December 31, 1951.)

Los Angeles

Chairman....R. D. Abbott (R. D. Abbott Co., Los Angeles). *Associate Chairman*....R. L. Short (Kirkhill Rubber Co., Los Angeles). *Vice-Chairman*....D. C. Maddy (Harwick Standard Chemical Co., Los Angeles). *Secretary*....F. C. Johnston (Caram Manufacturing Co., Monrovia, Calif.). *Treasurer*....C. S. Hoglund (R. D. Abbott Co., Los Angeles). (Terms expire December 31, 1951.)

New York

Chairman....M. R. Buffington (Lea Fabrics, Inc., Newark, N. J.). *Vice-Chairman*....J. S. Corrigall (R. T. Vanderbilt Co., New York). *Secretary-Treasurer*....B. B. Wilson (*India Rubber World*, New York). (Terms expire December 31, 1951.)

Northern California

Chairman....J. B. Watson (Goodyear Rubber Co., San Francisco). *Vice-Chairman*....Neil McIntyre (Oliver Tire and Rubber Co., Oakland.) *Secretary*....Grover Ramsey (Grove Regulator Co., Oakland). *Treasurer*.... James Sanford (American Rubber Co., Oakland). (Terms expire December 31, 1951.)

Philadelphia

Chairman....H. J. Reid (Gilmer Division, U. S. Rubber Co., Philadelphia). *Vice-Chairman*....T. W. Elkin (Armstrong Cork Co., Lancaster, Pa.). *Secretary-Treasurer*....George Wyrough (R. E. Carroll Co., Trenton). (Terms expire at meeting in January 1952.)

Rhode Island

Chairman....F. V. Newman (Respro, Inc., Cranston, R. I.). *Vice-Chairman*....C. L. Kingsford (Davol Rubber Co., Providence). *Secretary-Treasurer*....R. G. Volkman (U. S. Rubber Co., Providence). (Terms expire at Fall meeting of 1951.)

Southern Ohio

Chairman....L. J. Keyes (Dayton Rubber Co., Dayton). *Vice-Chairman* ....J. E. Feldman (Inland Manufacturing Division, General Motors Corp., Dayton). *Secretary*....R. J. Hoskin (Inland Manufacturing Div., General Motors Corp., Dayton). (Terms expire December 31, 1951.)

Washington, D. C.

Chairman....Warren Stubblebine (Office of the Quartermaster-General, Dept. of the Army, Washington). *Vice-Chairman*....T. R. Scanlan (Gates Rubber Co., Washington). *Secretary*....R. E. Harmon (Connecticut Hard Rubber Co., Washington). *Treasurer*....E. G. Holt (Office of Domestic Commerce, U. S. Dept. of Commerce, Washington). *Recording Secretary*.... (Miss) Ethel Levene (Bureau of Ships, U. S. Navy Dept., Washington). (Terms expire October, 1951.)

BYLAWS
of the
DIVISION OF RUBBER CHEMISTRY
AMERICAN CHEMICAL SOCIETY

I.

These Bylaws of the Division of Rubber Chemistry (hereinafter called "The Division") are subject to the Constitution and Bylaws of the American Chemical Society, and supersede all motions, rules, and bylaws of any nature whatsoever previously enacted by The Division which are in conflict herewith.

II. Members and Associates

The Division shall consist of:

(a) *Members*

Any person who is a member of the American Chemical Society may, on application, become a member of The Division by payment of the annual dues of two dollars and fifty cents ($2.50). Only members shall have the right to vote; only members entitled to hold office under the provisions of the Constitution and Bylaws of the American Chemical Society shall have the right to hold office in The Division. Members within the United States shall be entitled to receive "Rubber Chemistry and Technology" without additional cost, but foreign members shall pay an additional mailing charge as may be prescribed by the Treasurer. Membership is automatically terminated if the current yearly dues of the American Chemical Society and The Division are not paid by January 15.

(b) *Division Associates*

Any person, whether eligible or not for membership in the American Chemical Society, may, on application and acceptance, become an associate. The annual dues for Division associates shall be five dollars ($5.00). Associates are not members of the American Chemical Society and are not entitled to its privileges or to vote and hold office in The Division. Associates within the United States shall be entitled to receive "Rubber Chemistry and Technology" without additional cost, but foreign associates shall pay an additional mailing charge as may be prescribed by the Treasurer. Associate participation is automatically terminated if the current yearly dues are not paid by January 15.

III. Officers

The Officers of The Division shall be a Chairman, a Vice-Chairman, a Secretary, and a Treasurer, elected from the eligible membership of The Division. The duties of the Officers shall be those usually pertaining to their offices, and such other duties as may from time to time be delegated to them.

The elected Vice-Chairman at the expiration of his term of office shall become Chairman of The Division.

The Secretary, in addition to regular duties, with the assistance of the Papers Committee, shall arrange the papers program for the semiannual meetings. An announcement of the time and place of each meeting shall be mailed by the Secretary to each member, associate, and subscriber to "Rubber

Chemistry and Technology" not less than ninety (90) days prior to each meeting.

The Secretary, the Treasurer, and the Editor of "Rubber Chemistry and Technology" shall be bonded in amounts to be determined from time to time by the Executive Committee.

The Treasurer shall obtain the approval of the Executive Committee before making investments of the funds of The Division. The Treasurer shall maintain deposit accounts only in banks which have been approved by the Executive Committee.

IV. Directors

The Directors of The Division shall consist of, first, as many elected directors as there are sponsored Rubber Groups and, second, the outgoing chairman and the defeated vice-chairman candidate having the highest number of votes. The latter two directors shall serve for one (1) year, but those directors elected from the sponsored Rubber Groups shall serve two (2) years. One (1) director shall be elected from the eligible members of The Division located in the area served by each sponsored Rubber Group as hereinafter provided in Section VII, "Elections".

(In 1950, half of the directors elected from the sponsored Rubber Groups shall be elected for a term of one (1) year only, and the other half for two (2) years. In 1951, the term of all directors elected from the sponsored Rubber Groups shall be two (2) years. In 1950, the directors elected for a two (2)–year term shall be from the six (6) areas which have sponsored Rubber Groups with the greater length of sponsorship. The directors elected from the remaining younger Rubber Groups shall serve for one (1) year, but their successors elected in 1951 shall serve for two (2) years.)

V. Executive Committee

The Executive Committee shall consist of the officers and directors of The Division and the Editor and the Advertising Manager of "Rubber Chemistry and Technology". The Executive Committee shall be responsible for determining the general policy of The Division and for all specific duties herein provided.

The officers of the Executive Committee shall be the same as the officers of The Division.

The Executive Committee shall have the authority to fill by appointment any vacancy in the Executive Committee which may occur and such appointment shall continue in effect until the next regular election.

The Executive Committee shall have the authority to appoint two (2) councilors and two (2) alternate councilors to represent The Division at the council meetings of the American Chemical Society to serve two (2) years each, starting in alternate years. Councilors shall not be voting members of the Executive Committee unless appointed from that body or subsequently elected to it, but are expected to meet with the Executive Committee whenever possible. Either alternate may serve for either councilor.

Each director shall have the privilege of nominating an alternate who is a member of The Division to represent him, subject to the approval of the Chairman, at a meeting of the Executive Committee. The approved alternate director shall have the right to vote on all matters considered by the Executive Committee.

Meetings of the Executive Committee shall be called at least twice a year. Executive Committee meetings shall be called at the time and place of the general meetings of The Division and at such other time and place as the Chairman may designate.

Seven (7) members of the Executive Committee shall constitute a quorum.

VI. Steering Committee

The Steering Committee shall be comprised of the Chairman, Vice-Chairman, past Chairman, Treasurer, and Secretary of The Division. The Steering Committee shall be responsible to and report to the Executive Committee and shall have the authority to function for the Executive Committee in the interim between regular meetings of The Division in all matters which are not specifically designated in these bylaws as the responsibility of the Executive Committee.

VII. Elections

The Chairman of The Division shall, prior to March 1, appoint a Nominating Committee, consisting of a chairman and four (4) other members. The Nominating Committee shall submit, during the business session of the Spring Meeting, if said meeting is held, and, if not, to the Secretary, who will mail to each member, a slate nominating two (2) eligible members of The Division for Vice-Chairman, one (1) eligible member for Secretary, one (1) eligible member for Treasurer, and two (2) eligible members for Director for each area containing a sponsored Rubber Group for which there is an election to be held. The Nominating Committee shall obtain from the sponsored Rubber Group at least two (2) recommendations for the director to which the area served by each Rubber Group is entitled in that year. It shall be the duty of the Nominating Committee to make sure that area nominees for directors are eligible members of The Division.

In the event that no Spring Meeting of The Division is held, the Secretary shall announce the composition of the slate by publication in the rubber trade journals and in "Chemical and Engineering News". The Nominating Committee shall supply the Secretary with a short biographical sketch of each nominee and advise the Secretary that the nominees will serve, if elected. The membership shall have the opportunity of making additional nominations from the floor, or by letter, provided they are sponsored by at least twenty-five (25) members. Following the Spring Meeting and not later than forty-five (45) days before the time of the Fall Meeting, a printed ballot containing all the names, along with a short biographical sketch of nominees, arranged in alphabetical order for each office, shall be mailed by the Secretary to each member. A returned ballot to be valid must be postmarked not later than twenty (20) days before the time of the Fall Meeting, or before September 1, if no meeting is scheduled. The ballot shall be enclosed in an unmarked envelope, which in turn shall be enclosed in a mailing envelope on which appears the member's name and address.

The Chairman shall appoint a Teller's Committee, composed of a Chairman and two (2) other members, who shall receive the unopened legal ballots from the Secretary about fifteen (15) days before the Fall Meeting of The Division. The tellers shall count and tabulate the ballots and make a formal report at the business session of the Fall Meeting, announcing the successful candidates.

The Chairman shall not be eligible for reëlection, but automatically becomes

a director in The Division for the ensuing year. No nomination for chairman is to be made by the Nominating Committee unless the incumbent vice-chairman cannot serve as chairman, in which case the Nominating Committee shall nominate two (2) members for chairman.

A director shall not be eligible for reëlection to two (2) consecutive terms.

Each member may vote for a vice-chairman, a secretary, a treasurer, and one (1) director nominated from each area served by a sponsored Rubber Group.

In the event of an indecisive vote because of a tie for any office, those nominees receiving the tie votes shall be voted on by the members present at the Fall Meeting until the tie is removed. In the event that there is no fall meeting, the tie shall be removed by the vote of the outgoing Executive Committee. The elected officers and directors shall take office at the close of the Fall Meeting, or if no fall meeting is held, on October 1, and shall serve for the period of their elected terms or until their successors are elected.

VIII. Rubber Groups

The Executive Committee of The Division may sponsor groups within the rubber industry comprised of persons, whether chemists or not, who are interested in holding meetings where mutual problems may be discussed. The Executive Committee shall receive applications from any such proposed groups and shall decide whether or not The Division shall sponsor them.

The Executive Committee at its discretion may rescind the sponsorship of any group at any time by majority vote.

Membership in a Rubber Group of itself does not entitle a person to any more privileges in the American Chemical Society or The Division than the person would enjoy without Rubber Group membership.

The sponsored groups may indicate their relationship to The Division by the use of the following wording on letterheads and membership cards:

..... Rubber Group
Sponsored by the
Division of Rubber Chemistry
American Chemical Society

(The rules of the American Chemical Society do not permit the use of the Society's insignia or seal in this connection.)

The area served by each sponsored Rubber Group is entitled to one (1) elected director of The Division to serve for two (2) years. Whenever a new group is officially sponsored, the Steering Committee is empowered to appoint, subject to ratification by the Executive Committee at the next meeting of the Committee, a member to serve as interim director for the area of that group on the Executive Committee until the next general election.

To further the maintenance of a close relationship between The Division and sponsored Rubber Groups it shall be one of the duties of the Vice-Chairman of The Division to act as liaison officer between The Division and the sponsored Rubber Groups. The Vice-Chairman shall be assisted by a committee appointed by the Chairman. The Vice-Chairman shall transmit in writing each year to the Chairman of each sponsored Rubber Group information regarding the status of the sponsored groups and their relationship to The Division as prepared by the Committee on Sponsorship with the recommendation that this information be broadcast to the Rubber Group membership.

IX. "Rubber Chemistry and Technology"

The Division shall publish a journal entitled "Rubber Chemistry and Technology" (hereinafter referred to as "The Journal").

Companies and libraries may make application and, on acceptance, may subscribe to The Journal at the rate of five dollars ($5.00) per calendar year. Those subscribers located in foreign countries shall pay an additional mailing charge as may be prescribed by the Treasurer.

The Editor and Advertising Manager shall be appointed by the Chairman, subject to the approval of the elected members of the Executive Committee. Any such action shall be effective for no longer than one (1) year from the date of appointment and each shall serve until his successor is appointed.

The Editor shall publish The Journal quarterly during the year, in the name of The Division. He shall submit a budget for the following half of the calendar year to the Treasurer in writing, at least thirty (30) days before each regular meeting of the Executive Committee, and the Treasurer shall send copies of the budget to each member of said committee before the meeting.

The Editor and Advertising Manager shall absent themselves from Executive Committee meetings during discussion of the respective appointments of the Editor and Advertising Manager of The Journal.

The Division shall neither publish nor sponsor any other publication except on the approval of the Executive Committee and under the terms prescribed by them.

X. Budget

The fiscal year of The Division shall be September 1 to the following August 31.

Ten (10) days prior to each regular meeting of the Executive Committee, the Treasurer shall submit to each member of the Executive Committee, a proposed budget covering all contempleted expenditures for the following half of the fiscal year.

The Executive Committee at each regular meeting shall adopt a budget for The Division for the following half of the fiscal year.

The Treasurer shall pay out no funds of The Division in excess of said budget until ten (10) days after mailing notification to each member of the Executive Committee of the fact that the budget is to be exceeded, and no funds shall be paid in excess of the budget in the event that the Treasurer receives a written protest from three (3) members of the Executive Committee within ten (10) days of the date of said mailing, exclusive of Saturdays, Sundays, national holidays, and the date of mailing.

XI. Meetings

Regular semiannual meetings of The Division shall be held at the time and place selected for the meeting of the American Chemical Society unless the Executive Committee decides that the interest of The Division can better be served by holding the meeting at another location, or that no meeting be held. In case a location is selected other than that of the American Chemical Society Meeting, the time of the meeting of The Division shall be at least one month earlier or later than the American Chemical Society Meeting. The Chairman of The Division shall appoint a member of The Division resident in the locality where the meeting is to be held, who shall act as Chairman of the Local Com-

mittee on Arrangements, and select as many assistants as he may deem desirable to conduct the meeting.

The Local Chairman on Arrangements shall make to the Treasurer a financial report of the meeting of The Division.

The Division is responsible for financing each meeting of The Division, and therefore moneys collected by local committees to defray expenses of meetings of The Division shall be regarded as the property of The Division and shall be used to defray the expenses of the meeting for which the funds were obtained and any funds remaining after the defrayment of expenses of meetings shall be paid into the Treasury of The Division.

Fifty (50) Members shall constitute a quorum for any business meeting of The Division.

XII. Appointed Committees

The Chairman shall appoint the following committees and such other committees as from time to time he may deem necessary. These committees shall report at the semiannual meetings of The Division unless otherwise provided. The appointed committees shall serve during the term of the Chairman of The Division who made the appointment, but are subject to replacement at the pleasure of the Chairman.

(a) *Nominating Committee*

The composition and principal duties of this Committee have been heretofore set forth in Section VII, "Elections". In addition to the provision of that section, it shall be the duty of the Nominating Committee to determine whether the nominees are members in good standing of the American Chemical Society and of The Division, and to determine whether the nominees are willing to accept office, if elected.

It shall also be the duty of the Nominating Committee to furnish the Secretary with a short biographical sketch of each nominee.

(b) *Auditing Committee*

An Auditing Committee of three (3) members shall be appointed who shall make an annual audit of the books of The Division.

(c) *Finance and Budget Committee*

A Finance and Budget Committee of three (3) members shall be appointed to make recommendations to the Executive Committee regarding the handling and disposition of Division funds.

(d) *Membership Committee*

A Membership Committee of at least fifteen (15) members shall be appointed.

(e) *Papers Reviewing Committee*

One (1) member shall be appointed to serve with the Editor of "Rubber Chemistry and Technology", Chairman of The Division, and the Secretary as a Papers Reviewing Committee.

(f) *Nomenclature Committee*

A Nomenclature Committee of at least five (5) members shall be appointed to consider and make recommendations to The Division relative to naming of materials and terminology used by the rubber industry.

XIII. The Charles Goodyear Medal

1. The Charles Goodyear Medal, in commemoration of the discoverer of the vulcanization of rubber, may be awarded annually to a person who has made a valuable contribution to the science or technology of rubber or related subjects.

2. The Medal shall be awarded to a person selected by the Medal Committee. The Medalist shall also receive a scroll and an honorarium of two hundred dollars ($200.00).

3. The Executive Committee of The Division shall constitute the Medal Committee, and any meeting of the Executive Committee may be regarded as a meeting of the Medal Committee.

The Chairman of the Medal Committee shall be the immediate past Chairman of The Division.

Seven (7) members shall constitute a quorum.

4. The Medal Committee may make a nomination by an affirmative vote of the majority of those present at a meeting of the Committee. The nomination shall include not only the name of the individual nominated but also a statement as to the reason for his nomination.

5. If a member or members of the Executive Committee are proposed for nomination either by members of the Committee or by a member of The Division, such person or persons shall retire from the Committee while it is sitting as the Medal Committee and may be replaced by other members of The Division to be designated by the Chairman of the Medal Committee.

6. The persons to be considered for nomination shall include those whose names have been submitted to the Secretary of The Division by any member of The Division subsequent to the award of the next previous Charles Goodyear Medal. The Secretary shall, prior to the Spring Meeting of the Executive Committee, solicit names of proposed nominees from the members and shall circulate a list of all names collected to the members of the Executive Committee at least two (2) weeks before the date of the announced meeting of the Committee.

7. Within one (1) week after the nomination, the Secretary of The Division shall notify the candidate of his nomination, with the reasons therefor. On receipt of the candidate's acceptance of the nomination, the nomination shall thereby automatically become an election. Until the candidate accepts the nomination, the nomination shall not be made public. In case the candidate does not accept the nomination, the Committee may make another nomination.

8. Presentation shall be at a regular meeting of The Division by the Chairman, past Chairman, or other officer of The Division who shall be selected by the Executive Committee of The Division.

9. Acceptance of the nomination by the person nominated to receive the Medal shall be understood to require (a) the personal attendance of the recipient at a designated meeting of The Division at which the Medal is to be awarded, and (b) the delivery of a lecture before The Division at such meeting unless these provisions are specifically waived by the Executive Committee.

XIV. Responsibility

The Division shall not be held responsible for unauthorized opinions of its members, no matter how or where expressed.

XV. Amendment of Bylaws

Amendments may be proposed by any member by petition in writing to the Secretary, who shall refer such proposal to the Executive Committee. The Executive Committee shall consider the petition if it is endorsed by five (5) other members, and make recommendations to The Division during the business session of its next regular meetings. If a vote on the proposed change is called, then a two-thirds (2/3) favorable vote of the members present at the regular meeting shall be required for its adoption.

Approved
April 20, 1950

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY WASHINGTON, D. C., FEBRUARY 28 AND MARCH 1–2, 1951

The 58th Meeting of the Division of Rubber Chemistry was held in Washington, D. C., February 28 and March 1–2, 1951, with headquarters at the Hotel Shoreham. The total registration was six hundred and sixty-seven, anf five hundred and ninety-three attended the banquet on March 1. One hundred and twenty-four were present at the 25-Year Club Luncheon.

Five technical sessions were held, namely, Wednesday afternoon, Thursday morning and afternoon, and Friday morning and afternoon. Chairman Fielding made the opening remarks, and twenty-eight papers were presented. In addition, the Thursday afternoon session comprised a symposium on current problems concerned with rubber, as shown on the following program.

The following papers were presented:

(1) Sorption of 41° and 122°F GR-S Type Polymers with Carbon Blacks. JUNE DUKE AND W. K. TAFT (Government Laboratories, University of Akron) AND I. M. KOLTHOFF (University of Minnesota, Minneapolis).

(2) Influence of Adsorption by Carbon Black on the Oxidation of Unvulcanized Cold Rubber. C. W. SWEITZER AND F. LYON (Columbian Carbon Co., Brooklyn, N. Y.).

(3) Autographic Technique with Carbon-14 in Rubber. A. D. KIRSHENBAUM, C. W. HOFFMAN, AND A. V. GROSSE (Research Institute, Temple University, Philadelphia).

(4) Differentiation between Carbon Blacks by Electrical Resistance of Vulcanizates. J. E. MCKINNEY AND F. L. ROTH (National Bureau of Standards, Washington).

(5) Transmission of Mechanical Vibrations through Various Rubbers. R. E. MORRIS, ROBERT JAMES, AND H. L. SNYDER (Mare Island Naval Shipyard, Vallejo, California).

(6) Statistical Mechanics of Rubber. F. W. BOGGS (General Laboratories, U. S. Rubber Co., Passaic, N. J.).

(7) Banbury Mixing of Zinc Oxide. H. C. JONES AND E. G. SNYDER (New Jersey Zinc Co., Palmerton, Pennsylvania).

(8) Studies on Improving Silicone Rubber. A. C. GLIME, N. A. DUKE, AND C. M. DOEDE (Connecticut Hard Rubber Co., New Haven).

(9) Sulfonyl Hydrazide Blowing Agents for Rubber and Plastics. A. HUNTER AND D. L. SCHOENE (Naugatuck Chemical Division, U. S. Rubber Co., Naugatuck, Conn.)

(10) Cure Studies of some Aromatic Aldehydeamines. W. B. Shetterly (Naval Research Laboratory, Washington, D. C.).

(11) Rate of Cure of Present Day Whole-Tire Reclaimed Rubber, J. M. Ball and R. L. Randall (Midwest Rubber Reclaiming Co., East St. Louis, Illinois).

(12) Tread Wear of Tires. Influence of Type of Rubber and Black. J. Mandel, M. N. Steel, and R. D. Stiehler (National Bureau of Standards, Washington).

(13) Analysis of Nonskid Loss Mileage Data in Tread Wear Evaluations. D. G. Stechert and T. D. Bolt (Gates Rubber Co., Denver, Col.)

(14) Symposium on Current Rubber Problems. (i) The Government Rubber Program, E. G. Holt (Rubber Division, National Production Authority, Washington); (ii) Preparedness in Rubber. Arthur Wolf (Rubber Division, National Security Resources Board, Washington); (iii) The Army's Need for Rubberlike Materials. W. G. Stubblebine (Chemistry and Plastics Section, Office of the Quartermaster General, Washington).

(15) Lignin-Reinforced Nitrile, Neoprene, and Natural Rubbers. J. J. Keilen, W. K. Dougherty, and W. R. Cook (West Virginia Pulp & Paper Co., Charleston, S. C.).

(16) Method for Evaluating the Dynamic Fatigue of Adhesion of Tire Cords to Rubber Stocks. W. J. Loyns (Firestone Tire & Rubber Co., Akron).

(17) Migration of Materials during Accelerated Aging by the Oxygen Pressure Method. M. B. Fackler and J. S. Rugg (Gates Rubber Co., Denver, Colo.).

(18) Nondestructive Rubber Aging Tests. R. F. Shaw and S. R. Adams (Ordnance Corps., Dept. of the Army, Washington).

(19) Application of Infrared Spectrographic Methods in the Study of Ozone Deterioration of Rubber and Elastometric Materials. I. J. Stanley and A. R. Allison (New York Naval Shipyard, Brookly, N. Y.)

(20) New Method for the Quantitative Analysis of Natural Rubber Hydrocarbon. R. J. Fanning and Norman Bekkedahl (National Bureau of Standards, Washington).

(21) Determination of Rubber Hydrocarbon by an Improved Bromination Method. W. J. Gowans and F. E. Clark (U. S. Dept. of Agriculture, Albany, California).

(22) Viscosities of 0.25 to 90 Per Cent GR-S Rubber Solutions. A. B. Bestul, H. V. Belcher, F. A. Quinn, and C. B. Bryant (National Bureau of Standards, Washington).

(23) Determination of the Physical Properties of Natural and Synthetic Rubber Materials at Low Temperatures. J. Z. Lichtman and C. K. Chatten (New York Naval Shipyard, Brooklyn, N. Y.).

(24) Modulus and Relaxation of Elastomers in Torsion at Low Temperatures. W. E. Wolstenholme and M. Mooney (General Laboratories, U. S. Rubber Co., Passaic, New Jersey).

(25) Butadiene Polymers and Copolymers for Low Compression Set in Low-Temperature Service. R. E. Morris, J. W. Hollister, and F. L. Shew (Mare Island Naval Shipyard, Vallejo, California).

(26) Amine Activators for 5° C Emulsion Copolymerization Reactions. R. Spolsky, W. H. Embree, and H. L. Williams (Polymer Corporation, Ltd., Sarnia, Ontario).

(27) Reactivity of Butadine in Emulsion Copolymerization at 5° C. C. C.

WALLING (Lever Brothers, Cambridge, Mass.) AND J. A. DAVISON (General Laboratories, U. S. Rubber Co., Passaic, N. J.)

(28) Polymerization of 2,3-Difluorobutadiene and 2-Chloro-3-fluorobutadiene. L. B. WAKEFIELD (Firestone Tire & Rubber Co., Akron).

(29) Measurement of Refractive Index of Elastomers. AURELIA ARNOLD, IRVING MADORSKY, AND L. A. WOOD (National Bureau of Standards, Washington).

Business Meeting

Chairman J. H. Fielding, presiding.

The members were notified of the death of two of our members since the previous meeting:

Henry B. Morse — Endicott Johnson Corp.
Leon T. Wilson — American Wringer Co.

The Chairman reported that he had appointed thirteen committees, with a total of eighty members.

Amos W. Oakleaf was ratified as Assistant Treasurer, and F. W. Stavely and A. M. Neal were elected Councilor and Alternate, respectively, for 1951–52.

Drs. van Rossem and Houwink sent letters of appreciation to the Chairman of the Cleveland meeting for the courtesies extended them at the 57th Meeting.

The committee which has been investigating the financial condition of the Division recommends for the present no increase in dues, but this matter is going to be looked into intensively from the standpoint of reduction of expenses wherever possible.

At the fall meeting, D. E. Jones will be Local Chairman in charge, and the Hotel Commodore will be headquarters of the Division. There will be five Symposium meetings, starting Wednesday, September 5, and finishing Friday afternoon, September 7.

Membership Committee.—J. F. Kerscher reported that his committee has representatives on all groups and that the membership on February 1 was 2053, of which 1756 were regular and 297 associate members. This total increased during the month and is now 2077.

NEW BOOKS AND OTHER PUBLICATIONS

RUBBER IN AMERICA BEFORE 1492. Godfrey L. Cabot, Inc., 77 Franklin St., Boston 10, Mass. 12 pages.—This is an informal historical account of ancient American rubber uses and applications, written by J. Eric S. Thompson, noted archaeologist. Applications discussed include balls, rubber soled shoes, rubber ponchos, rubber bulbs for syringes, and rubber covered idols, and they are presented in a very interesting manner. [*India Rubber World.*]

BIBLIOGRAPHY OF RECENT RESEARCH IN THE FIELD OF HIGH POLYMERS. Robert Simha, Irma G. Callomon, Mary Budge Gaughan, and Helen H. Jeppson. National Bureau of Standards Circular 498. 60 pages. For sale by the Superintendent of Documents, United States Government Printing Office, Washington 25, D. C. Price, 20¢.—This bibliography of classified references in the high polymer field is taken from American periodicals from January, 1946, through December, 1949, and from available foreign periodicals up to January 1, 1950. [*India Rubber World.*]

RUBBER—AN IMPORTANT STRATEGIC COMMODITY. Financial Department, Rotterdamsche Bank, Amsterdam, The Netherlands. 8 × 10½ in. 52 pp.—This handsome illustrated booklet presents an interesting recapitulation of the history of rubber and its increasing importance as a strategic commodity. The rapid growth of production and consumption from rubber's earliest uses is recounted, and the situation in which the product found itself after both World Wars is discussed. Attention is paid to the synthetic rubber industry, and the effect it has had, or will have, on natural rubber. This phase of the discussion takes the question up to the "rubber boom" of 1950, and its resultant effects. The rubber policy of the United States is also discussed, and comparisons made between the natural and synthetic product, particularly as to pricing policies. As rubber, as a raw material, is of great importance to The Netherlands, the economic implications underlying the commodity's sales and production are emphasized. The booklet concludes with a presentation of data on the status of the Dutch economy. [*The Rubber Age* of New York.]

BANBURY MIXERS. (Bulletin No. 189.) Farrel-Birmingham Co., Inc., Ansonia, Conn. 8½ × 11 in. 32 pp.—Up-to-date information about recent improvements in Banbury Mixer design and construction, new applications and new installation layouts is contained in this booklet. General descriptive matter and illustrations of all sizes of Banbury Mixers, including a table of sizes and capacities, cross-section and cutaway views showing details of construction, and layout drawings showing various methods of installation in combination with other machines are provided. Also described and illustrated are the new Uni-Drive Banbury mixers, which have been especially developed to take the heavier loads resulting from mixing tougher stocks at higher speeds. [*The Rubber Age* of New York.]

RUBBER GRADE CARBON BLACKS AT A GLANCE. United Carbon Co., Inc., Charleston 27, W. Va. 1 page.—This chart gives the trade names and types of carbon blacks made by United Carbon, Huber, Cabot-General Atlas, Johnson, Columbian-Binney & Smith, Phillips, Witco-Continental, Thermatomic, and Richardson. [*India Rubber World.*]

THE CHEMISTRY OF ACRYLONITRILE. American Cyanamid Co., 30 Rockefeller Plaza, New York 20, N. Y. Cloth, 6 by 9 inches, 95 pages.—This book gives detailed information on the different methods of synthesis of acrylonitrile; physical properties, including structure, stability, and handling precautions; chemical properties, including reaction chart, reactions of the nitrile group, reactions of the double-bond, cyanoethylation reactions, and polymerization reactions; applications, including adhesives, antioxidants, emulsifying agents, fibers, plastics, plasticizers, rubber, surface coatings, etc.; methods of analysis; and toxicity. A bibliography of 580 literature references is appended, together with a comprehensive subject index. [*India Rubber World.*]

INDUSTRIAL SOLVENTS. Second Edition. Ibert Mellan, Rheinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth 6 by 9 inches, 768 pages. Price, $12.—This new edition represents the most comprehensive treatment of industrial solvents available. Much progress has been made

in the manufacture and application of solvents since the original edition in 1939, and this new volume has been extensively rewritten and enlarged to cover these new developments. The original chapters on plasticizers, and graphic expression and interpretation have been deleted; while a new chapter has been added on safe handling of solvents. In addition, selected, bibliographies have been included in each chapter, and the data on solvents have been further correlated into a coherent system of discussion.

Theoretical aspects of solvents and solutions are covered in the first four chapters, as follows: nature of solution; solvents, latent solvents, nonsolvents; vapor pressure, evaporation rate, boiling point; and viscosity. Following a general chapter on industrial application of solvents, and the new chapter on safe handling, come individual chapters where more than 380 solvents grouped according to types are discussed in detail, including physical data, commercial uses, and applications. Solvent types include hydrocarbon solvents, halogenated hydrocarbons, nitroparaffins, amines, alcohols, furfural, ketones, acids, ethers, and esters. The inclusion of a large number of graphs and tables provides a rapid means of obtaining specific and comparative data on the solvents discussed. A bibliography of references for further reading is appended to the book, together with comprehensive author and subject indices. [*India Rubber World.*]

COLLOID CHEMISTRY, THEORETICAL AND APPLIED. Volume VII. Theory and Methods, Biology and Medicine, Technological Applications.—Collected and edited by Jerome Alexander. Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth, 6 by 9 inches, 748 pages Price, $15.—This newest addition to the well known series on colloid chemistry contains 43 papers contributed by international authorities. Although grouped into the three sections shown in the subtitle of the volume, the papers cover widely different fields. As such, they are especially valuable in providing a quick review of work in other fields that may prove applicable to the reader's field. The first section, Theory and Methods, comprises 11 papers covering the basic structure and behavior of matter at various structural levels. Of particular interest to the rubber and plastics industries are the following papers in this section: "Scattering by Inhomogeneous Materials", P. Debye and A. M. Bueche; "The Role of the Electric Double Layer in the Behavior of Lyophobic Colloids", E. J. W. Verwey; "The Effective Depth of the Surface Zone of a Liquid", J. W. McBain and J. C. Henniker; "Laws of Surface Tension as Evidence of Aggregates in Liquids,", G. Antonoff; "Newtonian Flow in Polymer Chemistry", A. K. Doolittle; and "Successive Levels of Material Structure", J. Alexander.

The second section, Biology and Medicine, includes 11 papers on proteins, enzymes, drugs, genetics, tuberculosis, blood types, and dental caries. The third section, Technological Applications, consists of 21 papers, including the following: "Sonic Agglomeration of Carbon Black Aerosols", C. A. Stokes; "Organophilic Clays", E. A. Hauser; "The Reclaiming of Elastomers", D. S. le Beau; "Chemical and Physical Modifications of Textile Fibers", H. C. Borghetty; "Cellophane", C. M. Rosser; "Protective Wrappings—British Approach", C. R. Oswin; "Packaging—American Problems", C. A. Southwick, Jr.; and "Freeze-Drying", E. W. Flosdorf. Bibliographies are appended to each paper, and the book includes comprehensive author and subject indices. [*India Rubber World.*]

HANDBOOK OF CHEMISTRY AND PHYSICS. Thirty-Second Edition. Charles D. Hodgman, editor in chief. Chemical Rubber Publishing Co., 2310 Superior Ave. N.E., Cleveland, O. Cloth, 4½ by 7¼ inches, 2899 pages. Price, $7.50.—This newest edition of the standard handbook contains some 335 pages of new and completely revised material. Major revisions involving complete resetting have been made in the table of isotopes; letter symbols and abbreviations; description of the elements; periodic table; properties of commercial plastics; organic analytical reagents; potentials of electrochemical reactions; properties of amino acids; surface tension; vapor pressure; dielectric constants; and plate and film speeds. New additions to the handbook include tables on steroid hormones; electron work functions of the elements; centigrade-kelvin temperature conversions; and scientific and engineering abbreviations and symbols. [*India Rubber World.*]

THE EFFECT OF CHEMICAL CHANGES IN THE RUBBER HYDROCARBON ON ITS OXIDIZABILITY *

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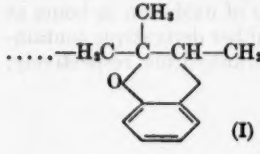
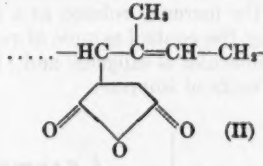
INSTITUT FRANÇAIS DE CAOUTCHOUC, PARIS, FRANCE

The hydrocarbon of rubber, which contains one ethylene linkage or double bond per isoprene unit, has such a structure that it is very sensitive to the action of oxygen, and the investigations of Farmer[1] have shown clearly the part played by the α-methylene carbon atom in the process of oxidation. Since the rubber hydrocarbon can be made to react with compounds which unite directly with it, an attempt was made to find out what influence any changes of this kind might have on the oxidiazbility of rubber.

The reagents chosen were saligenol and maleic anhydride. According to Cunneen, Farmer, and Koch[2], saligenol attaches itself to double bonds, with formation of a chromanic nucleus (I), the nature of which the present authors have examined and confirmed by ultraviolet spectrography of the compounds prepared. In the case of maleic anhydride, Delalande[3] has shown that this compound and also related compounds, such as maleic imide, can combine according to the substitutive addition mechanism described by Alder[4], with the formation of a molecule of type (II). The reactions were carried out with exclusion of air, in accordance with the technique of Moureu and Dufraisse[5] on benzene solutions of purified crepe rubber, and in the absence of a catalyst[6].



(I)



(II)

In this way modified rubber derivatives were prepared, which contained various proportions of saligenol (2.5 to 58 moles per 100 isoprene units), or of maleic anhydride (7 to 19 moles per 100 isoprene units), and the oxidizability of these products was measured at 80° C by the manometric method. The results are shown schematically in Figures 1 and 2.

Figure 1 shows the oxidizability (expressed as the ascent in mm. of the mercury column after oxidation for 10 hours) as a function of the number of molecules of reagent which combine per 100 isoprene units. It is at once evident that in neither case is the decrease in oxidizability proportional to the number of molecules which combine; in other words, in the case of saligenol, the decrease in oxidizability is not proportional to the percentage of double bonds which become saturated, and, in the case of maleic anhydride, the de-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Comptes Rendus des Séances de l'Academie des Sciences*, Vol. 231, pages 230–232, July 17 1950.

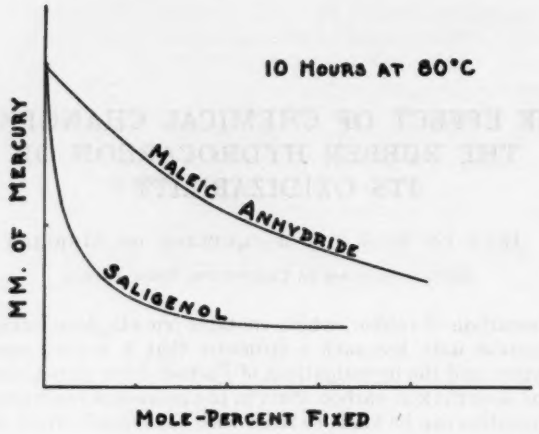


FIG. 1.

crease in oxidizability is not proportional to the percentage of α-methylenic carbon atoms which become blocked.

In addition to this, a decided difference in the course of the two curves in Figure 1 is evident, for saturation of the double bonds has a much greater influence, at least for a relatively small change in the rubber hydrocarbon, than does blocking of the α-methylenic carbon atoms. For this reason the oxidizability is reduced to one-half by the fixation of about 10 moles of maleic anhydride per 100 isoprene units, whereas fewer than 2 moles of saligenol are sufficient to give the same decrease in oxidizability.

Figure 2 shows curves of absorption of oxygen (expressed as the ascent in mm. of the mercury column as a function of the time of oxidation in hours at 80° C) by the control sample of rubber and by two rubber derivatives containing 11 molecules of saligenol and 11 molecules of maleic anhydride, respectively, per 100 units of isoprene.

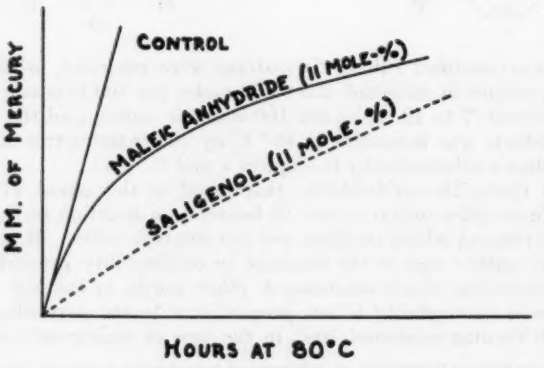


FIG. 2.

In the case of saligenol, the oxidizability is reduced from the very beginning of the oxidation process; on the contrary, in the case of maleic anhydride, the initial rate of oxidation is almost the same as that of the control rubber. This observation would seem to favor the hypothesis proposed by Farmer[7], according to which the oxidation reactions are initiated by the fixation of oxygen on the double bonds. It shows, in fact, that the initiation reactions would not be altered by blocking the α-methylenic carbon atoms, even if they were to be retarded by saturation of the ethylenic bonds.

It follows from these results that, on the one hand, chemical modifications of the rubber hydrocarbon may change in a notable way its behavior toward oxygen, and, on the other hand, that the way in which foreign molecules attach themselves to the macromolecules is of influence also.

REFERENCES

[1] See, for example, Farmer, Bloomfield, Sundralingam, and Sutton, *Trans. Inst. Rubber Ind.* **38**, 348 (1942).
[2] Cunneen, Farmer, and Koch, *J. Chem. Soc.* **472**, 6 (1943).
[3] Delalande, Thesis, Paris, 1947.
[4] Alder, *Ber.* **76**, 27 (1943).
[5] Moureu and Dufraisse, *Inst. intern. chim. Solvay, II^e Conseil de Chimie*, 1925, p. 578.
[6] The physical properties of the products obtained under such conditions would seem to warrant the assumption that the reactions take place without degradation of the molecule and, because there is no appreciable gelation of the solutions, without formation of intermolecular bridges.
[7] Farmer, *Trans. Inst. Rubber Ind.* **21**, 122 (1945).

EFFECT OF FILLERS ON PLASTICITY OF UNVULCANIZED RUBBER *

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INTRODUCTION

The process of plasticizing unvulcanized rubber is second only in importance in the rubber industry to that of vulcanization, and knowledge of the flow properties of the unvulcanized material is essential to the proper control of subsequent processing operations, a matter discussed fully in a previous paper[1]. Despite this, the dependence of the flow properties on plasticizing treatments and the effect of compounding ingredients is not well understood, though a beginning has been made with the study of the former[2]. This report describes an investigation into the rheological properties of dispersions of fillers in rubber; most of the work deals with carbon black, the most important filler in the rubber industry, and thus extends previous work on carbon black in vulcanized rubber[3].

Solid fillers may cause considerable changes in the plasticity of rubber stocks. The stock is usually stiffened to an extent which depends on the relative volume added, but there are pronounced differences in plasticity between stocks containing similar volumes of different fillers; in particular, reinforcing carbon blacks produce large increases in stiffness. The plasticity of a mixed stock thus depends on both the volume concentration of the filler and the nature of the filler particles, as well as on the plasticity of the rubber matrix. Early work by Blow, Depew, Stamberger, Twiss and others has been ably summarized by Shepard, Street and Park[4], while a selection of more recent work is given in other publications[5].

Often compounded rubber stocks show evidence of thixotropic behavior, if allowed to stand they may become progressively stiffer, only to soften again during working. Although behavior of this type has been widely recognized and possible causes have been discussed, there is still a lack of information on its consequences in plasticity measurement.

Important features of fillers which may govern their effect on the properties of rubber stocks are the size and shape of their particles, and the chemical nature and structure of their particles and particle surfaces. Before addition to rubber, the fillers exist as coarse powders composed of clusters or aggregates of primary particles. During incorporation into the rubber these aggregates are broken down to a size which depends on the severity and nature of the dispersing technique; in the limiting case—presumably rarely reached—every primary particle may be completely isolated from its neighbors. The sizes of the primary particles are usually such that they are well below the limit of resolution of optical microscopes, and thus estimates of the dispersion or breakdown of aggregates are obtained by measuring the physical properties of the mixtures. Electron microscope studies have been shown to be of value in in-

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 27, No. 1, pages 55–74, February 1951.

vestigations on the nature of these dispersions, but unfortunately sufficient work has not yet been undertaken.

EXPERIMENTAL

So far, detailed investigation has been confined to rubber stocks without vulcanizing ingredients, so as to avoid complications due to scorching during the plasticity measurements. However, the effects described are generally similar in stocks containing sulfur. The base mixes were simple dispersions of filler in rubber, but in some mixes a third component was added to modify the dispersion.

The results in Sections 4 and 5 were obtained on masticated smoked sheet (Mix A, see below) or on an M.P.C. carbon black stock (Mix B). These stocks were masticated for as nearly as possible the same time and under similar conditions; they were heavily masticated because it was found that this reduced a complication, due to the rubber matrix, shown by lightly milled stocks. Lightly masticated smoked sheet showed thixotropic behavior and evidence of a weak structure which was readily broken down by shearing, but which complicated the behavior of lightly milled black stocks. With heavily masticated materials the influence of this rubber matrix structure was much less pronounced.

The behavior of lightly masticated stocks containing M.P.C. black (Mix C), a variety of other fillers, and other compounding ingredients, is considered in Sections 6 and 7.

The compounding and mixing details for the stocks used in most of this investigation are given below. They were mixed on a 12 × 6-inch laboratory roll mill, with the temperature of rolls nominally 52° C. The batch size was approximately 3 pounds.

Mix A. Smoked sheet; mastication time 80 minutes.
Mix B. Smoked sheet 100 parts, M.P.C. black 40 parts; total mastication and mixing time 80 minutes.
Mix C. Smoked sheet 100 parts, M.P.C. black 40 parts; total mastication and mixing time 10 minutes.

In all cases the proportions are in parts by weight. It was necessary to repeat certain of these mixings, and slight differences were found in the plasticity values of these repeat batches, but results which are compared directly in this report were obtained on the same batch.

Plasticity measurements were made on the modified Mooney shearing disc plastometer described by Piper and Scott.[13] This uses a biconical rotor, which gives a substantially uniform rate of shear throughout the rubber. The four rates of shear employed, 10, 1.0, 0.1 and 0.01 per second, will for convenience be referred to as Rate 10, Rate 1, Rate 0.1 and Rate 0.01, respectively. Measurements of the shearing torque were recorded at intervals during continuous shearing of the stocks, which were maintained at 100° C. Owing to some uncertainty as to the location of the effective surface of the grooved rotor and dies and to nonuniformity in the edge zone, the shear rates quoted above can only be considered as nominal. For the same reasons an exact calculation of the shear stress corresponding to a given torque is difficult, and, moreover, is not necessary for the purposes of this report; accordingly only the torque readings are given, in arbitrary units, but as a rough guide 200 of these units may be taken to correspond to a shear stress of 10^6 dynes per sq. cm.

DISCUSSION OF RESULTS OF PRELIMINARY EXPERIMENTS

Preliminary experiments showed that the rheological properties of rubber stocks depend on their past history; their properties may be changed continuously on the one hand by shearing and on the other hand by standing. Furthermore, as the properties may be changed during the act of measurement, care is needed in interpreting the test results. In view of this dependence of the properties on the whole past history of the rubber, it is essential, if comparable series of measurements are to be obtained, that each experimental result should be obtained either on a separate sample of the material with a history as similar as possible to that of previous samples, or on material brought to a reproducible reference state before each series is undertaken.

For convenience the history of the samples can be divided into the following four stages:

Stage A:—*Storage.*—This occurs during the period between mixing and conditioning (Stage B), and may be at normal or other temperatures. (Unless otherwise stated, storage was at normal room temperature.)

Stage B:—*Conditioning.*—This involves shearing the samples at 100° C until they are brought to a reproducible condition; it eliminates some of the differences due to dissimilar storage.

Stage C:—*Recovery.*—In this stage the samples are allowed to rest after conditioning (Stage B), recovery taking place in the plastometer at controlled temperatures. During "recovery" there is an increase in stiffness, which may continue until the material is stiffer than initially.

Stage D:—*Testing.*—This is the measurement of the torque required to shear the sample continuously, all measurements being made at 100° C.

It was found that with all the stocks here examined continuous shearing for 20 minutes at the highest rate available—Rate 10—was sufficient to bring the plastic properties to a level which enabled adequately reproducible measurements to be made at the three lower rates of shear, and thus made the effects of differences in their past history negligible, provided that the stocks had not been stored before test for widely different periods. This conditioning technique was adopted in all the measurements in which it was necessary to bring the stocks repeatedly to a reproducible state.

The changes in plasticity resulting from mechanical treatment (conditioning or testing) or from standing (recovery) can be attributed to a *breakdown* or a *growth* of *structure*, respectively, the former showing itself as a decrease and the latter as an increase in the torque required to shear the rubber at a given rate. These terms will be used freely in the following discussion, but at this stage they are not identified with any specific type of structure.

GROWTH OF STRUCTURE

SERIES I

To study the growth of structure at 100° C, samples were conditioned by shearing for 20 minutes at the highest rate of shear, Rate 10, and were then allowed to recover at 100° C. Torque-time curves were recorded at a lower rate of shear (Rate 1) after various periods of recovery. Figure 1 shows typical families of curves for the masticated smoked sheet (Mix A) and the M.P.C. black stock (Mix B). For clarity, the rapid rise in torque to its peak value is not shown; this rise is usually completed during the first five seconds' shearing.

These sets of curves show a number of interesting features. With both the masticated smoked sheet and the black loaded stock, the torque during con-

tinuous shearing may either fall or rise before reaching an approximately steady value. Curves which were commenced five seconds after conditioning, *i.e.*, as soon after as possible, show a rise in the torque during the first few minutes of shearing, while the curves obtained on samples that had recovered for longer periods show that standing at 100° C leads to a progressive increase in the initial torque required subsequently to shear the material. This increase is attributed to a growth of structure during the recovery period. With masticated smoked sheet this increase completely disappears after a very short period of shearing; with the black stock the increase is much more pronounced and more prolonged.

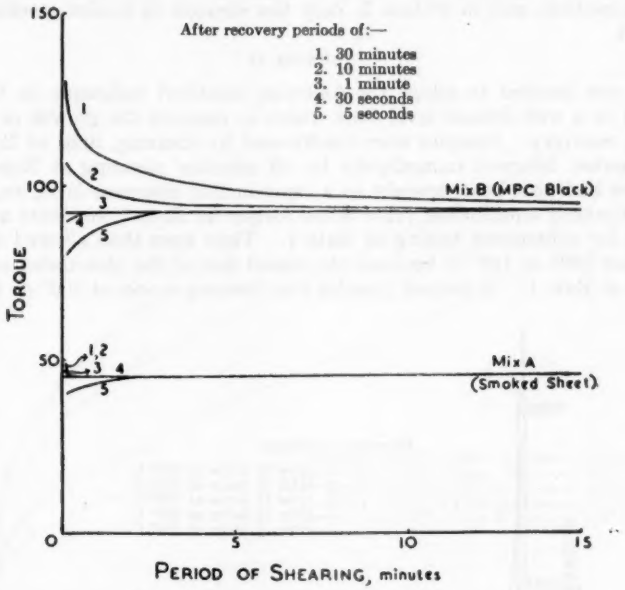

FIG. 1.—Recovery after previous shearing.

It appears that at least two processes occur during continuous shearing of rubber stocks; first, a growth in structure which causes the torque to increase, and, secondly, a breakdown in structure which leads to a decrease in the torque. A steady value of the torque is reached when the rate of growth equals the rate of breakdown, and this steady state can be considered as a *dynamic equilibrium*.

The curves obtained after very short periods of recovery at 100° C approach this steady value from below. Two processes may contribute to this increase of torque; one is a growth of structure during the actual measurement; the other is due to a small rise of temperature which occurs when the stock is sheared at the highest rate. This increase in temperature softens the stock, and a reduction of the rate of shearing causes a small decrease in temperature, which shows itself as an increase in torque. During shearing at rates lower than Rate 10, the temperature rise is negligibly small.

After about a minute's recovery at 100° C the difference between the structure in dynamic equilibrium at the test shear rate (Rate 1) and the struc-

ture present immediately after the conditioning at Rate 10 has already been repaired; more prolonged recovery leads to a growth of structure in excess of the Rate 1 equilibrium value, and this excess is broken down during the test at this rate.

Although both the masticated smoked sheet and the black stock show changes due to thixotropic structure that can either be broken down or built up, the changes in the smoked sheet are very small compared with those in the black stock. With lightly masticated smoked sheet these effects are more evident, but it is found that the structure is substantially broken down during the first 15 seconds' shearing. It appears that in the black stock most of the structural changes occur because of the presence of the filler; in the remainder of this section, and in section 5, only the changes in loaded stocks are considered.

SERIES II

It was decided to adopt the following modified technique so that there should be a well defined level from which to measure the growth of structure during recovery. Samples were conditioned by shearing, first, at Rate 10 for 20 minutes, followed immediately by 10 minutes' shearing at Rate 1. The samples had now been brought to a reproducible reference level, namely, the approximately equilibrium value of the torque for Rate 1, and were now conditioned for subsequent testing at Rate 1. They were then allowed to recover at either 100° or 120° C between the closed dies of the platometer and finally tested at Rate 1. It seemed possible that keeping stocks at 100° or 120° C for

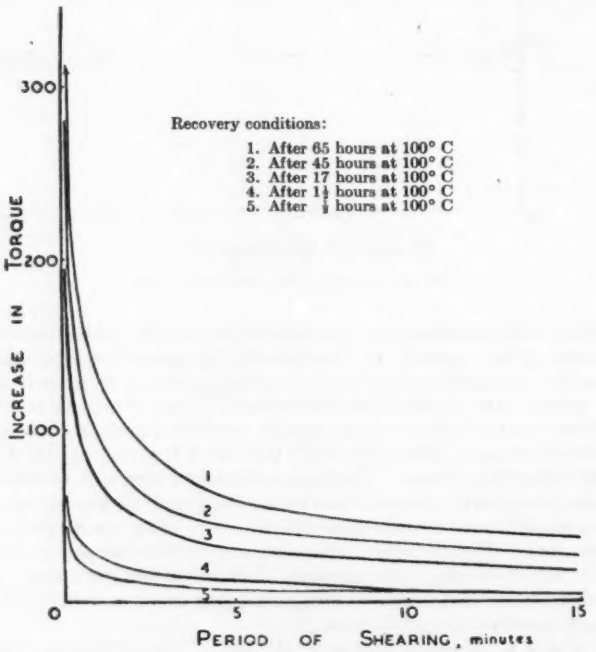

FIG. 2.—Recovery at 100° C.

extended periods might cause serious degradation of the rubber hydrocarbon and thus cause an appreciable change in the flow properties of the rubber stock. It was found that, although exposure of Mix B in an open oven caused considerable softening of the rubber, heating between the closed dies of the plastometer for periods up to 92 hours did not cause any important change in the reference level attained after Rate 10 shearing referred to above. It thus appears that fresh supplies of oxygen are effectively excluded from the rubber in the plastometer.

The differences between the ordinates of the time-torque curve at Rate 1 after recovery and the equilibrium torque for Rate 1 were then used to give an indication of the growth in structure. Figure 2 shows a family of curves ob-

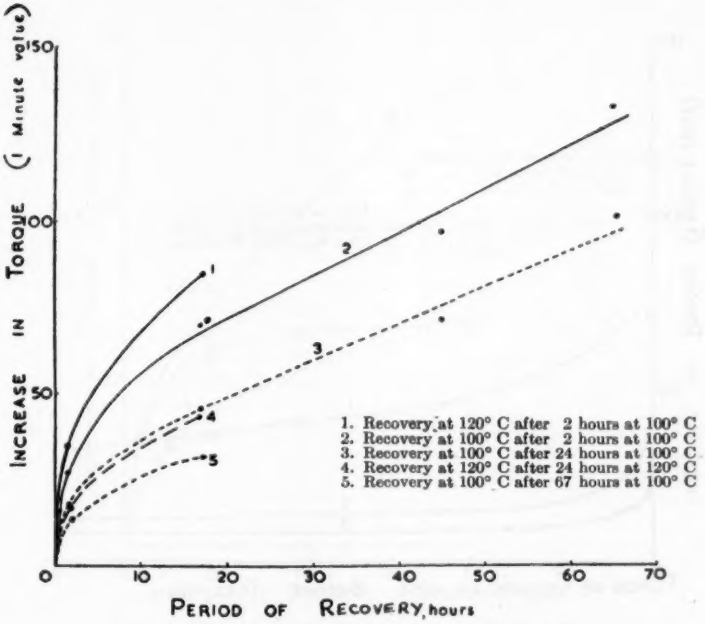

FIG. 3.—Effect of temperature and recovery period on recovery.

tained in this way for the black stock (Mix B). The shapes of all the curves are very similar and thus the growth of structure during each period of recovery can conveniently be represented by a single number. The difference between the torque after 1 minute's continuous shearing and the equilibrium value was found to be convenient to characterize the degree of stiffening which had occurred during recovery. This choice of the 1-minute value was made so that any structure due to the rubber hydrocarbon would have been broken down but considerable filler structure would remain; the increase of this 1-minute value above the equilibrium value is, therefore, used as an index of filler structure.

The increase in the 1-minute value of torque is plotted against period of recovery in Figure 3. The two full lines represent the growth of structure occurring during the continuous recovery of stock which had been maintained at

100° C for 2 hours (comprising storage and shearing to the reproducible reference level) before recovery commenced. These curves show a progressive growth of structure with period of recovery, the rate of growth being increased as the temperature is raised. The conditioning before, and measurement after, the 120° C recovery were at 100° C, the temperature being raised and lowered as rapidly as possible, so that the 100° and 120° C curves are strictly comparable.

The dotted lines in Figure 3 show the results of tests on samples which had been previously stored in the plastometer at 100° C for 24 or 67 hours; these show a much slower rate of growth of structure. It appears that standing at elevated temperatures, besides producing a growth in structure, results also in a decrease in the ability of the material subsequently to form structure. The

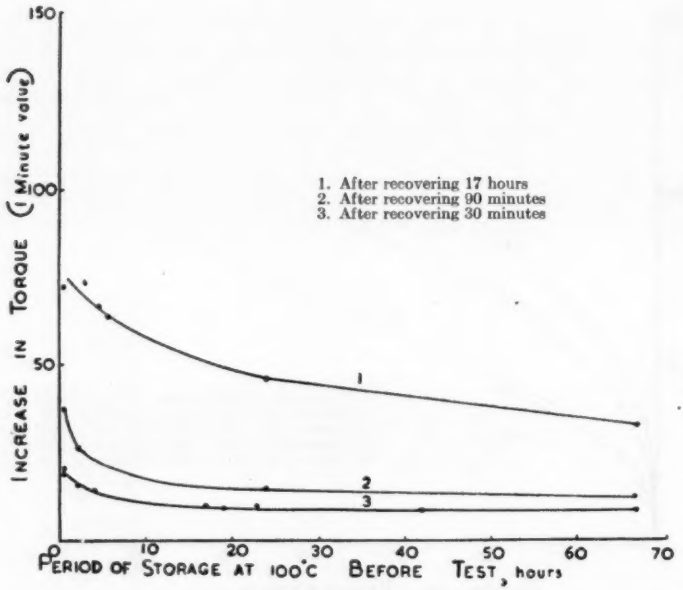

FIG. 4.—Influence of period of storage on recovery.

broken line (curve 4) in Figure 3 refers to material which was stored for 24 hours at 120° C before measurements were commenced, and subsequently allowed to recover at 120° C. It will be seen that structure forms less readily than after 24 hours' storage at 100° C and subsequent recovery (after mechanical conditioning) at 100° C (curve 3), and thus it appears that the ability to form structure is reduced more rapidly by storage at 120° than at 100° C.

This falling off in structure-forming ability as a result of exposure to elevated temperatures is shown in a different way in Figure 4. Here the structure-index (the increase in the 1-minute value of the torque), measured after three different periods of recovery at 100° C, is plotted against the period of storage at 100° C before commencement of the tests. It is found that the falling off in the ability to form structure depends on the total time at 100° C before the rub-

ber is conditioned for the test, and is substantially independent of the strain-history before this conditioning.

SERIES III

So far we have described only the growth of structure during recovery, *i.e.*, with the rubber stock at rest. During shearing the two processes of growth and breakdown of structure occur simultaneously, and so the net increase in structure during shearing is less than that during recovery at rest. To follow the change of structure under these conditions samples were conditioned in the way described in earlier experiments on growth of structure, *i.e.*, 20 minutes, shearing at Rate 10 followed by 10 minutes' shearing at Rate 1, and then some of the samples were allowed to recover at 100° C while others were continu-

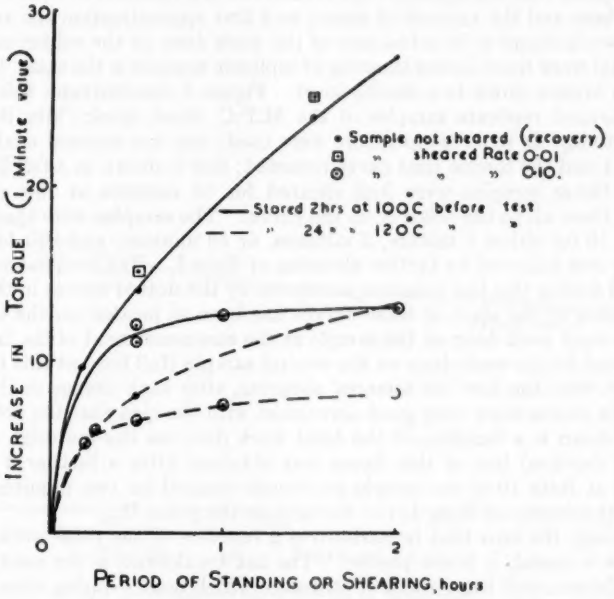

FIG. 5.—Effect of rate of shearing on recovery.

ously sheared at one of the two lower shear rates. After various selected periods of recovery or shearing, the structure present was assessed, as in the previous experiments, by shearing at Rate 1 and determining the structure index, *i.e.*, the difference between the 1 minute value of the torque and the equilibrium value at Rate 1. In Figure 5 the change in this index of structure with period of recovery at rest or with period of shearing is shown for samples stored for 2 hours at 100° C before the tests (full lines) and for samples stored for 24 hours at 120° C (broken lines). With both samples the rate of formation of structure immediately after commencing the recovery or low-speed shearing appears to be independent of the rate of shear. As the amount of structure increases towards that for equilibrium at Rate 0.1, the curve for this rate becomes flat. At Rate 0.01 it was not possible to distinguish between the curves obtained by

shearing at this low rate and recovery at rest even after 2.5 hours. In the material stored longer at a high temperature, and so rendered less active for structure formation, the equilibrium structure at Rate 0.1 is reduced in about the same ratio as the extent of formation of structure at rest—an effect which might be anticipated from the concept of dynamic equilibrium discussed above.

BREAKDOWN OF STRUCTURE

It was mentioned in the previous section that both a growth and a breakdown of structure occur during the continuous shearing of rubber stocks, and to account for the apparently smaller amount of structure present after shearing at higher rates it was suggested that breakdown was more rapid at these higher rates.

It appears that the apparent net breakdown is a function of both the torque during shear and the amount of shear; to a first approximation the amount of breakdown is found to be a function of the work done on the rubber stock, *i.e.*, if the total work done during shearing of replicate samples is the same, then they are both broken down to a similar level. Figure 6 demonstrates this dependence. Several replicate samples of the M.P.C. black stock (Mix B) after 6 weeks' storage at room temperature were used; one was sheared continuously at Rate 1 and the torque time curve recorded; this is shown as a full line in the figure. Other samples were first sheared for 10 minutes at this rate; this brought them all to the point A on the curve. The samples were then sheared at Rate 10 for either 1 minute, 2 minutes, or 10 minutes, and this high-speed shearing was followed by further shearing at Rate 1. The torque-time curves obtained during this last shearing are shown by the dotted curves in the figure; the position of the start of these curves has been so located on the time scale that the total work done on the sample at the commencement of the last shearing is equal to the work done on the control sample (full line) at this time.

Apart from the first few minutes' shearing, after each change in the rate of shear, the curves show very good agreement with the idea that the net amount of breakdown is a function of the total work done on the material. The remaining (broken) line of this figure was obtained after a further 2 minutes' shearing at Rate 10 of the sample previously sheared for two minutes at Rate 10 and 24 minutes at Rate 1, *i.e.*, brought to the point B.

Although the idea that breakdown is a function of the total work done on the stock is useful, it is not precise. The net breakdown is the result of both the breakdown and the growth of structure which occurs during shearing, and we have already shown that the ability to form a structure decreases with continued exposure to high temperature. This decrease would obviously result in less structure being formed in samples which have been sheared for a long period than in those sheared for a short period, even if the actual breakdown of structure were the same in both cases.

The results in Figure 6 apply only to samples with identical history, and it must not be supposed that the rate of breakdown for stocks with different histories (even if they have been exposed for similar periods at elevated temperatures) is a function only of work. Were this so, we should expect that the rate of breakdown at one shear rate would be a function of torque only and that this is not so is clear from Figure 2. The rate of breakdown, judged by the slope of the curves at a particular value of torque, depends on the period at 100° C (recovery) before shearing, *i.e.*, varies from curve to curve in Figure 2. This behavior is not surprising, as we should expect the structure formed on

standing to include a wide range of bond strengths, and assuming that on shearing the bonds broken initially are predominantly the weaker ones, the average strength of bonds at a particular value of torque is greater for samples which had been allowed to stand for longer periods (the upper curves of Figure 2).

A closer study of the torque-time curves obtained during continuous shearing of rubber stocks at constant rate shows that the approximately steady state to which reference has already been made is not a true dynamic equilibrium, and that a slow decrease in torque still continues, even though shearing is continued for extremely long periods. Thus it is important to recognize that all previous mention of an equilibrium or steady state refers only to an approximately steady value of the torque which appears to exist in experiments that are

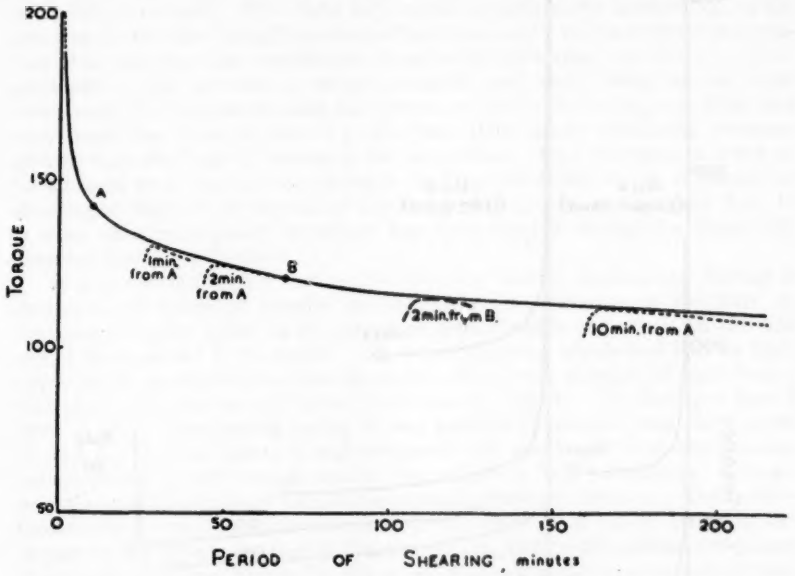

FIG. 6.—Breakdown due to shearing at various rates.

sufficiently prolonged for much of the breakdown to have taken place, but also sufficiently short so that the slow continuous breakdown is not an appreciable contribution to the measured breakdown.

We can now contrast the structures in masticated smoked sheet and the black loaded stocks. First, in smoked sheet the structure is readily broken down by a short period of shearing and apparently is weak; it quickly reforms on standing, and, after only 10 minutes at 100° C it has almost reached its maximum value; this corresponds to an increase of not more than 20 per cent in the torque required to shear the material. The formation of this structure is not influenced by prolonged storage at 100° C. With the M.P.C. black stocks the structure is much stronger and is only relatively slowly broken down by shearing; on standing it reforms continuously; even after 67 hours at 100° C, it still shows a steady rate of increase; after this period the torque required to

shear the stock may exceed the initial value by a factor of five or six. Further, the ability of the structure to reform is decreased by previous storage at elevated temperatures.

BEHAVIOR BEFORE MECHANICAL CONDITIONING

The experiments in Section 4 were carried out on stocks which had been brought to a reproducible reference level by shearing before the commencement of the tests. It is obviously of practical interest to follow the changes which occur during the testing of material which has not been subjected to this conditioning treatment.

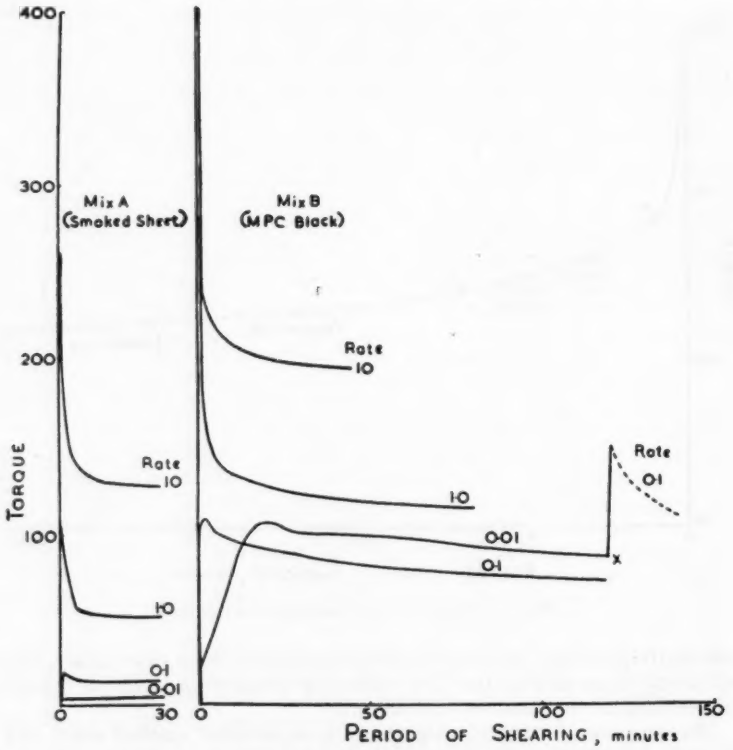

FIG. 7.—Effect of shear rate on shape of torque-period of shear curves.

Figure 7 gives torque-time curves obtained at each of the available shear rates for samples of both Mix A and Mix B; the samples were sheeted from the mill as thin sheets, stored at room temperature (10 to 15° C) for about 3 weeks and were then heated in the plastometer for 1 minute at 100° C before the commencement of shearing. The appropriate curves in this figure should be contrasted with those in Figure 1.

Comparing first the curve obtained on smoked sheet at Rate 1 with the curves obtained after conditioning and recovery (Figure 1), the initial peak in the torque-time curve is now much higher, and the torque does not fall as rapidly to a steady value. However, when the sample was heated in the plastometer for an hour or more at 100° C before testing, the initial peak was much less pronounced. The reasons for this behavior have yet to be investigated, but the influence of changes in the preheating period suggests that the existence of the high peak cannot be entirely due to the rubber being non-uniform in temperature. The curves obtained on the smoked sheet at other shear rates also have a similar form.

For the M.P.C. stock, the Rate 10, Rate 1, and Rate 0.1 curves differ from the corresponding smoked sheet curves in that the torque continues to decrease for a very long time, in accordance with the behavior to be expected from a stock with filler structure. The Rate 0.01 curve is particularly interesting, as the amount of structure initially present after storage for 3 weeks at room temperature was less than the equilibrium structure at this speed at 100° C. Consequently a slow increase in torque occurred, and since, owing to the lower shear rate, the amount of work performed on the rubber in a given time was very much less than at Rate 0.1, the Rate 0.01 torque eventually becomes greater than the Rate 0.1 torque at the same time. That the position is not as paradoxical as at first appears is made clear by the dotted curve, obtained by shearing at Rate 0.1 at the end of the Rate 0.01 run (*i.e.*, at the point X). It is clear that considerable structure has been formed during the Rate 0.01 shearing (compare Figure 5.)

It is to be anticipated that as the interval between mixing and testing is decreased, it would be possible to observe a net formation of structure on shearing at higher rates, as the structure present while the mix is on the mill would be expected to be small. To obtain material which had had as little opportunity as possible to form structure, Mix C was sheeted off thin from a laboratory mill into ice-cold water and stored at −10° C. On testing at Rate 1 after as short a preheating period as was possible (1 minute), the curve given by the full line in Figure 8 was obtained. It was hoped that this heating period would be sufficient to enable the rubber to heat adequately; a longer period would be necessary for complete temperature equilibrium. The torque-time curve shows (1) an initial peak and rapid decrease in torque probably due in part to incomplete heating of the mix, and in part to the rubber component of the mix (compare Figure 7); (2) a rise due to formation of structure; and (3) an eventual slow fall in torque.

The effect of increasing the time of preheating at 100° C before testing is, as might be expected, gradually to eliminate the initial dip, and cause considerable stiffening of the rubber (dotted curves). Room temperature storage for long periods followed by 1 minute's heating at 100° C (broken lines, Figure 8) causes a stiffening which eliminates the dip in the full line curve; however, this is accompanied by a general softening of the mix which lowers the reference level reached after considerable shearing at Rate 10 (results not shown in Figure 8), and causes the torque obtained at Rate 1 (broken lines, Figure 8) to fall below the value obtained on the unstored material (full line, Figure 8) after a few minutes shearing. A similar but less marked softening has been observed in other stocks on storage at 100° C for periods of about an hour before test at Rate 1, but in the case of Mix C, Figure 8, the increase in structure on storage at this temperature masks the softening effect, if it is present. This fall in reference level due to prolonged storage at room temperature is accompanied

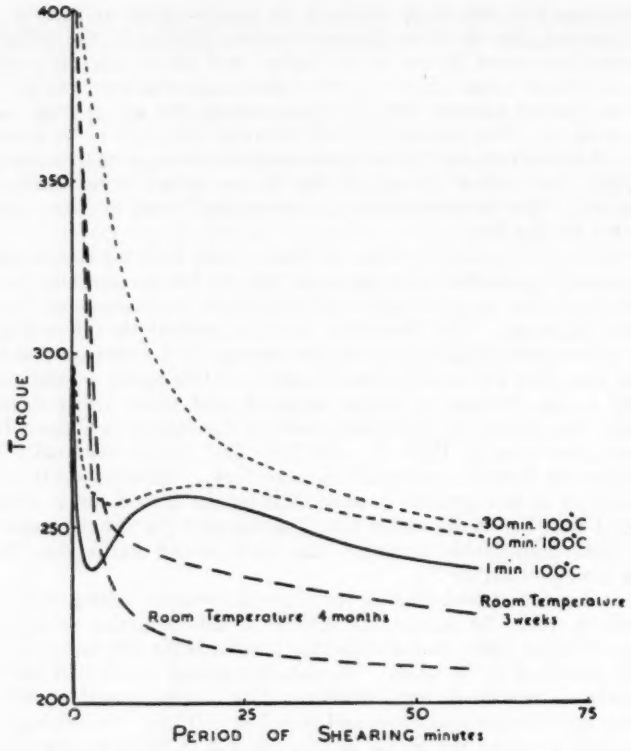

FIG. 8.—Influence of storage conditions on initial torque curve.

by a reduction in the ability of the structure to reform, and may be associated with the similar effect at elevated temperatures discussed above. However, there is not an exact parallel in results at the two temperatures, as is shown by the differences between the dotted and broken lines in Figure 8. It appears from this and from the results in Figure 3 that the formation of structure and the loss of ability to reform structure both occur more rapidly at elevated temperatures, but that an increase in temperature accelerates the formation of structure relative to the loss of ability to form structure. It should be noted that storage for 4 months at room temperature only very slightly affected the plasticity of lightly masticated uncompounded smoked sheet.

EFFECTS OF VARIOUS FILLERS

In the earlier sections of this paper we have considered only the effects of growth and breakdown of structure in masticated smoked sheet and M.P.C. black stocks. In this section the behavior of stocks containing a variety of fillers is described; these stocks contained 100 parts by weight of smoked sheet and 4 parts of stearic acid, together with similar volume loadings of one of the following fillers—M.P.C. black (40 parts), M.T. black (40 parts), U.F. black

(40 parts), Shawinigan black (40 parts), precipitated whiting (60 parts), and were masticated for similar periods. The stearic acid was added to the smoked sheet before the fillers so that any influence on dispersion would be as great as possible. The technique adopted to follow the growth of structure was similar to that used previously; the samples were conditioned by shearing for 20 minutes at Rate 10 followed by 10 minutes at Rate 1, and then torque-time curves during shearing at Rate 1 were recorded after various recovery periods at 100° C. As the ability to form structure is affected by the thermal history of the sample, it was arranged that all samples were at 100° C for 2 hours (comprising preliminary storage and conditioning) before the commencement of recovery.

Figure 9 shows the change of the torque with period of recovery, the value of the torque after 1 minute's shearing being plotted. The curves show that the stocks differ considerably in stiffness; the equilibrium value of the torque before any build-up of structure at 100° C is largest in the Shawinigan black stock and smallest in the M.T. black stock. The differences in this equilibrium value of the torque presumably correspond to differences in the amount of structure due to the filler which is not broken down by previous shearing. The

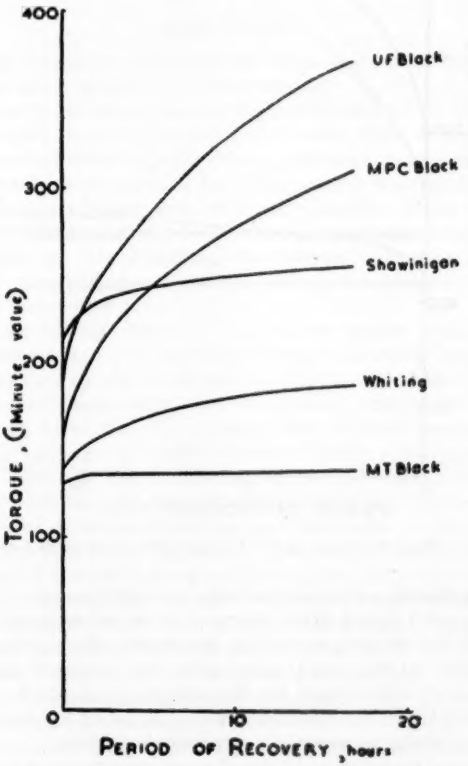

FIG. 9.— Influence of various fillers on structure formation.

Shawinigan black stock thus shows the greatest amount of this "permanent" structure and the M.T. black stock the least.

Secondly, the shapes of the various curves show pronounced differences; it will be remembered that an increase in the 1-minute value of the torque is associated with a growth in structure. Again the M.T. black stock shows the least activity and little structure growth during prolonged recovery at 100° C; the precipitated whiting shows a somewhat larger structure growth, but M.P.C. and U.F. blacks show considerable growth. The Shawinigan black stock shows little growth of structure during standing at this temperature; it appears

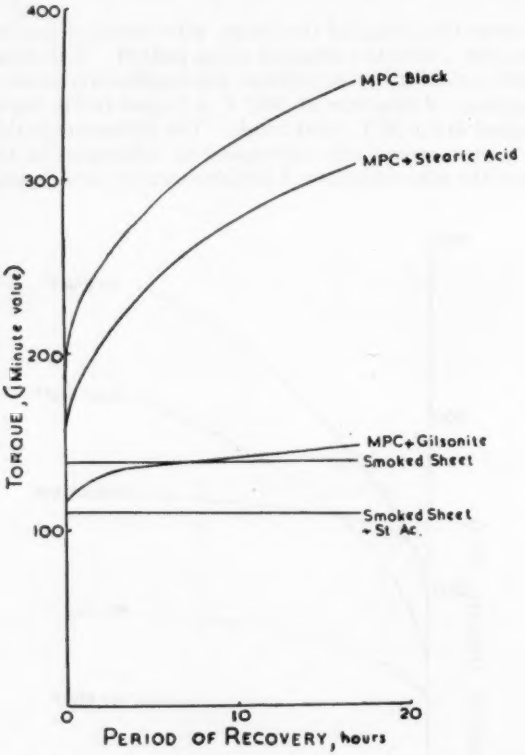

FIG. 10.—Effect of softeners in M.P.C. black stocks on structure formation.

that this black possesses a strong structure not easily broken down by shearing, *i.e.*, conditioning, and shows little reformation on subsequent standing. The M.P.C. and U.F. blacks possess weaker structures which are broken down by shearing and reform on standing; indeed after long recovery periods the structure in these stocks exceeds that in the Shawinigan black stock. The curves for the loaded stocks should be contrasted with the curve for masticated smoked sheet in Figure 10 where no growth in structure is evident.

It is well known that the addition of small quantities of various materials may greatly influence the rheological properties of dispersed systems; these

materials are adsorbed on to the surfaces of the particles and modify their activity. Another series of similar experiments was therefore carried out on M.P.C. black stocks with no addition, with stearic acid (4 parts), or with Gilsonite (10 parts).

The results are shown in Figure 10, together with those for masticated smoked sheet and a masticated smoked sheet to which 4 parts of stearic acid had been added, the mastication periods for all these materials being as similar as possible.

The effect of adding stearic acid is merely to soften the stock, as the actual increase in the shearing torque caused by adding black to masticated smoked sheet is not altered by the presence of the stearic acid, and, further, the rate of growth of structure during recovery at 100° C is unaffected by its presence. This evidence suggests that stearic acid merely acts as a softener during the compounding of M.P.C. black loaded stocks and does not modify the filler structure, and thus adds weight to the recent suggestion by Morris and Hollister[14] that stearic acid does not improve dispersion of carbon black. On the other hand, Gilsonite, besides softening the rubber stock, leads to a pronounced decrease in the ability of the black to form structure, presumably due to a modification of the surface of the black particles.

DISCUSSION

We are now in a position to discuss the ideas which have been put forward, and to give them some qualitative interpretation.

It appears that in all rubber stocks there is some kind of internal structure which can be broken down by shearing and which then reforms on standing. In masticated smoked sheet this thixotropic behavior can be explained by the disentanglement and orientation of the long chain rubber molecules produced by shearing. These readjustments result in a decrease in the torque required to shear the material at a constant rate, as the stearic hindrance to flow is reduced by orientation. On standing, the internal structure reforms as the molecules return to a random orientation, due to the constant thermal motion of the long chain molecules.

The thixotropic effects observed with rubber stocks containing fillers are much more pronounced. The amount of structure which can be built up or broken down may be expected to depend on the nature of the filler, its particle size, its structural characteristics, and its surface. Although there is no way of readily isolating them, there is evidence that at least two processes are responsible for this behavior in loaded stocks: (1) the orientation and (or) disentanglement of both the long molecular chains and anisotropic filler particles or chains of filler particles; (2) breakdown of interactions either between neighboring filler particles or between the filler and the rubber, or both. The first of these processes has just been discussed. The interactions or bonds will have a range of strengths, the breakdown of the weak bonds occurring more readily. On standing after shearing the structures reform at rates which depend on the temperature. The ability of a filler to form structure can be modified by the addition of small quantities of surface-active materials. The behavior described here shows a striking similarity to that shown by vulcanizates containing fillers. This similarity has been discussed more fully elsewhere[15].

The main problem in determining the effect of these phenomena on the behavior of rubber stocks during processing, and in the measurement of plasticity, is to predict the behavior of the material from a knowledge of its past history. It will be recognized that this task is difficult even in the simplest case when all

structural changes are reversible, but when irreversible processes are continuously taking place the problem becomes extremely complex.

Sweitzer, Goodrich, and Burgess[12] have recently described an interesting investigation into the "carbon black gel complex". Working with GR-S, they identify the benzene-insoluble rubber formed in unvulcanized carbon black compounds as "carbon gel", and discuss the effect of various mixing conditions on the formation of the gel. This gel, which results in both loss of solubility and stiffening of stocks, is presumably associated with the filler structure to which reference has been made in this paper and in earlier work[3,4,15]. Carbon gel determinations on natural rubber stocks have also been reported[16].

Information on the dispersion of particles in liquids has been obtained from measurements of the viscosity of suspensions. The basic theory relating viscosity to concentration of particles, which was developed by Einstein, has been extended by many investigators, and it is not unnatural that the possible use of this type of theory to account for the rheological properties of rubber should have attracted considerable attention. Smallwood[6], Rehner[7], Guth[8] and Cohan[9], have all employed theories of this type to account for the changes in viscous and stiffness properties of rubbers; experimental results which roughly conform to theory have been obtained and departures from the theoretical equations explained in a qualitative way.

Although the application of these theoretical equations to experimental results is not unpromising, it is often forgotten that the conditions under which the experiments are carried out and those assumed in the theory may be quite different. In particular, the presence of a filler structure which can be broken down or built up introduces complications to the simple application of these theories. For example, the curves in Figure 7 show that the proportionate stiffening caused by carbon black is much greater when determined at low rates of shear than at high rates.

Apart from an obvious need to condition samples so that reproducible results may be obtained, it is also essential to recognize that measurements although reproducible may not be characteristic. As mentioned above measurements of the equilibrium value of plasticity made at different rates of shear give different material constants.

It is evident that ideas on plasticity testing must be reviewed, taking into account the presence of filler structure, and we shall conclude this discussion by considering a number of practical consequences of the behavior reported above. If maximum information is to be obtained from the results of plasticity tests, it is important that either the complete history of the test-sample should be closely controlled, or the sample should be conditioned (before measurement) so that its properties are substantially independent of differences in previous history. However, this latter course may not be possible if the history of the samples is very dissimilar. Generally it will be found valuable mechanically to condition samples before measurement, the nature of the conditioning treatment depending on the use to which the results are to be put. The main purpose of any plasticity test is to assess the ease with which rubbers may be processed, and if information is required of the likely flow properties during the actual process, the conditioning treatment or the act of measurement should involve as severe a breakdown of filler structure as is involved in the technical process; obviously measurements on samples which have been subject to relatively little breakdown may be misleading. In addition, both the conditioning treatment and the measurement should be carried out at a temperature appropriate to this use, as comparative results obtained at one tem-

perature should not be used as a guide to behavior at another temperature. The different degrees of breakdown involved in measurements using a number of different types of plastometer, or the relative sensitivity of the results from different plastometers to filler structure, may be the source of anomalous results obtained in the comparison of stocks remilled for progressively increasing periods[17].

Finally, it is obvious that the normal scorch test carried out with compression plastometers requires overhaul; here the growth of filler structure is confused with the progress of vulcanization, and techniques which involve severe deformation before the test should be more informative of the scorching of the stock. The use of a shearing cone or disc plastometer generally overcomes these troubles, but care must still be exercised to distinguish filler structure from vulcanization. These criticisms applying to scorch tests which involve the measurement of plasticity also apply to tests which involve the swelling or dissolution of the stocks.

SUMMARY

An investigation into the effect of fillers on the flow properties of rubber stocks is described. It is shown that rubber stocks containing fillers soften on working and stiffen on standing, and these changes are associated with the breaking down and formation of some internal structure. The amount of this structure which can be broken down or built up in this way depends on the nature of the filler; it is most evident in stocks containing fine reinforcing carbon blacks, but the ability of the filler to form structure can be modified by addition of small quantities of surface-active materials.

The measured value of the plasticity of compounded rubber stocks is thus not a definite value characteristic of the stock, but depends on the whole past history of the sample, and a wide range of plasticity values may be obtained, depending on the history and the conditions of test. The practical significance of these results is discussed, and proposals which would assist the revision of ideas on plasticity tests are put forward.

ACKNOWLEDGMENT

The authors wish to thank the Council of the Research Association of British Rubber Manufacturers for permission to publish the results of this investigation carried out in the Association's laboratories.

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THE MECHANICAL ACTIVATION OF RUBBERS (OXIDATION UNDER MECHANICAL STRESS) *

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In the practical application of rubber products, their fatigue characteristics, *i.e.*, the rate of deterioration under repeated mechanical deformation, are frequently of wide importance.

Work by several authors[1] has established the fact that the fatigue effect increases significantly under the influence of oxygen, *e.g.*, the fatigue resistance of rubber in an atmosphere of oxygen is many times lower than in an inert medium.

It was found also that in the fatigue process, as in the thermal oxidation of rubber, the inhibitor is consumed[2].

The cause of the more rapid deterioration of rubber with fatigue is the subject of discussion of the present work. Until now the effect of mechanical stresses on the oxidation processes has not been accurately determined.

The present authors have investigated the effect of repeated deformations on the rate of oxidation of vulcanized butadiene-styrene rubber in different kinetic periods of the reaction (induction period, autocatalysis). In these experiments, particular attention was devoted to the microkinetics (kinetics of inhibited oxidation) of the inhibition method which was employed[3].

The latter was used in the investigations of the kinetics of the consumption of the inhibitor (phenyl-β-naphthylamine) in the oxidation of rubber. Since in thermal oxidation, this process follows a linear law, the kinetic curve with respect to the time axis gives the rate of reaction. The latter approximates the rate of the initial reaction between the oxygen and the rubber, that is, the rate of initiation of oxidation (W_i) if all the original active centers are eliminated by the inhibitor[4].

Figure 1 shows that, in the fatigue of vulcanizates at different temperatures, the consumption of inhibitor follows the same linear law.

From Figure 2 it is obvious that the rate of consumption (W_M) of the inhibitor (phenyl-β-naphthylamine) during fatiguing was greater than the rate (W_i) in the thermal processes.

Inasmuch as these values correspond to the rates of union of oxygen and rubber, the equation: $\Delta_W = W_M - W_i$, represents the supplementray rate which depends on the application of mechanical stresses. This exceptionally significant phenomenon is observed at various temperatures and at various states of deformation. Figures 2 and 3 show the effect on the rate of consumption of the inhibitor of different amplitudes and frequencies of deformation. It is evident that the greater the amplitude and frequency of deformation, the faster the union of oxygen with the double bonds of rubber proceeds. This rate depends directly on the amplitude and frequency of deformation (see Figure 4).

* Translated for Rubber Chemistry and Technology by Alan Davis from *Reports to the Academy of Science*, U.S.S.R., Vol. 71, No. 2, 319–22 (1950).

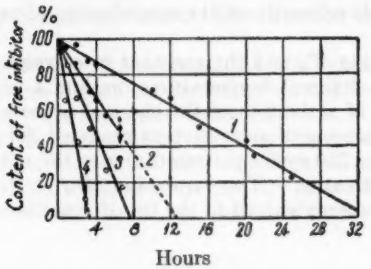

FIG. 1.—Kinetics of consumption of inhibitor without deformation and with fatigue (amplitude 50%, frequency 250 cycles per minute). (1) Without deformation (123° C); (2) with fatigue (123° C); (3) without deformation (143° C); (4) during fatigue (143° C).

It is possible to prove that the application of mechanical stresses on the vulcanizate induces the reaction of the oxygen, and that an increase in the stress increases the activation effect.

The possibility of this mechanical activation of rubber and its vulcanizates is evident by their very nature. Because of the considerable length of the molecules and the large number of relaxation times recorded, high stresses are imposed on various molecules and their particles during the course of the experiment. Besides, the whole range of relaxation times could not be realized if the value of the stress changed. This effect is particularly significant when the computed value of the stress in every cycle passes through zero.

Mechanical stress, applied to the molecular chains, tends to oppose the valence forces and, in certain units, may weaken the chemical bonds so much that it exceeds the activation barrier of the reaction. Mechanical rupture of the molecules also is possible. However, although the energy of oxidation is lower than the energy of dissociation of the hydrocarbon, every molecule in process of rupturing passes through a stage of activation.

Under conditions of repeated deformation of a vulcanizate, corresponding to static distribution, the active molecules are more numerous than mechanically rupturing molecules, since the distribution of energy depends on the deformation. We have shown that the most active units in the molecules of different rubbers are the double bonds of the main chains. The mechanical stresses are transmitted even to the main chains. Consequently the effect of

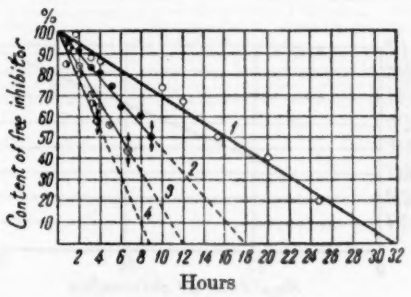

FIG. 2.—Influence of the amplitude of deformation on the kinetics of consumption of inhibitor during fatigue (123° C) and frequency 250 cycles per minute). (1) Without deformation; (2) amplitude 25%; (3) amplitude 50%; (4) amplitude 75%.

the activation depends primarily on the rate of union of oxygen with the double bonds.

Actually, computing W_i and the constant k_i corresponding to the rate for thermal oxidation at different temperatures, we find a value of 21 calories per mole[6] for the energy of activation of the thermal process E_T. Corresponding calculations for the process of activation at repeated deformations (amplitude 50 per cent, frequency 250 cycles per minute) give the value 18.1 kcal. per mole for the energy of activation. The expression: $E_M - E_T$, in this case 3 kcal per mole, represents energy gained in the transformation of mechanical energy to chemical energy[7].

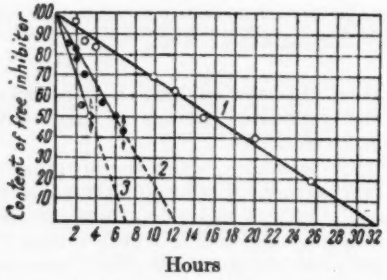

FIG. 3.—Influence of frequency of deformation on kinetics of consumption of inhibitor with fatigue (123° amplitude 50%). (1) Without deformation; (2) frequency 250 cycles per minute; (3) frequency 500 cycles per minute.

It is possible to make the calculations by another method, obtaining first the value of those rates which depend exclusively upon the mechanical activation Δ_W. The energy of activation of this process under the conditions assumed for the preceding calculation is 16 kcal. per mole.

At first glance it would appear possible to say that the basic cause of mechanical activation is mechanical rupture of the molecules. Nevertheless, not only is this viewpoint at variance with the statistical results obtained, it is also contradicted by the assumed higher energy barrier of mechanical activation. In fact, if mechanical activation were to be regarded as mechanical rupture, the first consequence of rupture would be the appearance of units of chain radicals. The latter would react with oxygen; hence the activation barrier of such a

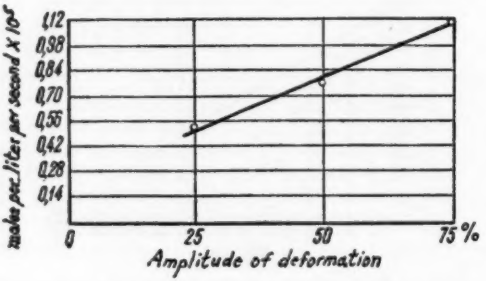

FIG. 4.—Influence of amplitude of deformation on the rate of initiation of oxidation during fatigue (123° C, frequency 250 cycles per minute).

reaction would be 5–8 kcal. per mole. This was not observed in the experiments.

In complete accord with the interpretation, the rupture of molecular chains in the absence of oxygen is significantly impeded, and the fatigue resistance of the vulcanizate greatly increases (see Table 1).

The facts which we have studied and have described concerning the mechanical oxidation of rubber have a broad significance. Mechanical activation causes a lowering of the fatigue resistance of vulcanizates and takes place during a series of processes in the production of rubber, *e.g.*, plasticization, vulcanization, etc.

TABLE I

RESISTANCE TO FATIGUE OF VULCANIZATES OF BUTADIENE–STYRENE RUBBER IN OXYGEN AND NITROGEN (FREQUENCY 250 CYCLES PER MINUTE, AMPLITUDE 50 PER CENT)

Temperature (° C)	Number of cycles to rupture (in 1000)		Relative resistance to fatigue
	n_0 (in oxygen)	n_N (in nitrogen)	n_0/n_N
20	90	180	2
40	45	190	4
60	20	200	10
80	7	195	28
100	2	210	105

Since mechanical activation represents a weakening of the chemical bonds between the atoms in the main chains of the rubber molecules, it follows that it facilitates the progress of a number of reactions between rubber and chemical agents. For example, the process of ozone-cracking of rubbers under stress is certainly mechanically activated. The effect is increased by the application of a different stress.

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[4] Vulcanizates of the following structure were investigated: 96.6% rubber; 3% tetramethylthiuramdisulfide; 1% ZnO; 0.4% phenyl-β-naphthylamine. The specimens were subjected to repeated deformations in a special apparatus constructed by the present authors.

[5] This conclusion is correct for an ideal inhibitor, in the presence of which all initial active centers become inactive. In the actual cases a certain portion of the initial active centers decline progressively while the molecular chains are disrupted. The probability of similar cases is very slight and they have no significance in the investigation of the kinetics of oxidation. However, for the values of the effectiveness of different inhibitors, it is impossible to ignore the proven phenomenon, since it shows an influence on the mechanical properties of the rubbers.

[6] By one mole of butadiene-styrene is meant the molecular weight of a structural unit containing one double bond, and the styrene is not taken into account, but is considered ballast. The concentrations were computed in moles per liter of rubber; the rates in moles per liter per second.

[7] The work was performed with thin sheets, and heating was practically excluded.

TETRAMETHYLTHIURAM DISULFIDE VULCANIZATION OF EXTRACTED RUBBER. I. INTRODUCTION AND COMPOUNDING *

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The scope of the present series of papers embraces a limited portion of the field of soft-rubber vulcanization, namely, vulcanization with tetramethylthiuram disulfide (TMTD) in the absence of added sulfur. However, for perspective, it has seemed desirable to include a minimum of work on simple sulfur vulcanization in the presence of accelerators. Our reason for investigating the thiuram disulfide type of cure stems from the relatively simple structure and behavior of the TMTD molecule when compared to the eight-membered-ring sulfur molecule. Thus, the reaction products, including those of macromolecular weight which occur in TMTD vulcanizates, might be fewer in number and simpler in structure than those occurring in accelerated sulfur vulcanizates.

The techniques which we have applied include short-path distillation and radiosulfur tracer chemistry. Certain applications of these will be described in the succeeding papers. The small-scale compounding methods described by Garvey[1] and modified to suit our purposes were used. Certain of the compounding features of our study were chosen to be reported in this introductory paper.

MATERIALS

One of the main purposes of the study was to isolate and identify the vulcanization products. Therefore more than usual care was taken in selecting and characterizing those starting materials which sometimes are of uncertain composition.

Rubber.—Preliminary experiments were conducted with crepe because of its recognized quality. Acetone-extracted crepe was chosen for later experiments mainly because of its low fat acid content. The stability in air of this material was believed sufficient.

Sulfur.—This element, according to Nier[2], contains 95% S^{32}, 0.74% S^{33}, 4.2% S^{34}, and 0.016% S^{36}. The radioactive sulfur, S*, used contained S^{35} as a tracer. The half-life of this isotope[3] is 87 ± 1 days. P^{32} was removed from the sample by oxidation to phosphoric acid with concentrated HNO_3. The sulfur was ground in a mortar, boiled with dilute Na_2CO_3, and recrystallized from styrene.

Analysis.—Calcd. for S_8: S, 100.00. *Found:* S, 100.07, 100.15.

* Reprinted from the *Journal of Polymer Science:* Part I from Vol. 5, No. 6, pages 709–717, December 1950; Part II from Vol. 6, No. 1, pages 1–5, January 1951; Part III from Vol. 6, No. 1, pages 7–11, January 1951; Part IV from Vol. 6, No. 1, pages 13–20, January 1951; Part V from Vol. 6, No. 2, pages 177–187, February 1951.

Fat Acid.—Palmitic acid was chosen because of its occurrence as a major component in the fat acid used in compounding. The sample selected for this study was Eastman Kodak White Label, m.p. 63°.

Zinc oxide.—A reagent grade French process sample was used for chemical reactions, while pigment grade French process material was used for compounding.

Zinc sulfide.—This material was reagent grade.

Analysis.—*Calcd. for ZnS:* Zn, 67.1; S, 32.9. *Found:* Zn, 67.3, 67.3; S, 32.35, 32.20.

Zinc palmitate.—This salt was prepared as described in Part IV of the present series.

Tetramethylthiuram disulfide or TMTD.—For most of the compounding studies, a commercial grade containing about 3 per cent hydrocarbon oil was used. It melted at about 155°. By recrystallization from alcohol in the presence of a little sulfur or from benzene, the melting point was raised to 159–160°, with decomposition. The preparation of radioactive TMTD is set forth in Part II of this series.

Tetramethylthiuram monosulfide or TMTM.—The commercial material melting at about 107° was used for compounding. A sample after recrystallization from alcohol melted at 109–110°. It was bright yellow.

Zinc dimethyl dithiocarbamate or ZnDMDC.—The commercial salt melting at 243–245° was used.

The abbreviation phr is used for "parts per hundred of rubber", TMTU for tetramethylthiourea, DMADC for dimethylammonium dimethyldithiocarbamate, and PBNA for phenyl-beta-naphthylamine.

LITERATURE

Usually the assumption due to Bruni and Romani[4], but studied also by Bedford and coworkers[5], is made that one of the four sulfur atoms of TMTD is available for effecting vulcanization. This assumption finds support in the fact that TMTM does not vulcanize rubber in the absence of added sulfur, although Cummings and Simmons[6] reported that 4.333 phr TMTM +0.667 phr sulfur is equivalent to 5.00 phr of TMTD for the vulcanization of rubber containing 5.00 phr of zinc oxide. These investigators opined that this behavior supported the contention of Bedford and Gray[7] that TMTD is active as the result of the formation of ZnDMDC. Clark, LeTourneau, and Ball[8] detected this salt *in situ* in vulcanizates. Jarrijon[9] effectively used a somewhat obscure ultraviolet absorption technique for the quantitative analysis of acetone extracts. He found that 70–76 per cent of the TMTD (3 phr) added to a zinc oxide (2 phr) stock could be accounted for as ZnDMDC. The spectrographic results were verified by a gravimetric procedure. Jarrijon found that either acetone-extracted or deproteinized rubber vulcanized satisfactorily with TMTD, provided zinc oxide was present. He considered that fat acids were not necessary and that vulcanization occurred only when ZnDMDC was formed. Shephard[10], previous to the above work, demonstrated by color reactions that the zinc salt was formed during vulcanization, and this was confirmed by Shimada[11]. Morrison and Shephard[12] quote Cotton and Westhead[13] (erroneously) to the effect that fat acids are required with TMTD, and suggest that lack of H_2S formation with extracted rubber would prevent vulcanization. Hydrogen sulfide in small amounts was considered necessary by Bedford and Gray in that it effected the formation of ZnDMDC. They considered H_2S to be an inhibitor of vulcanization if present in excess of the amount required to

convert the TMTD to ZnDMDC. The products of the latter reaction were reported to be zinc sulfide, CS_2 and dimethylammonium dimethyldithiocarbamate.

Most investigators[14] consider that zinc oxide is either necessary or desirable for the development of the best physical properties. The minimum quantity mentioned by Morrison and Shephard is 1 phr but they prefer 5 phr. However, Bedford and Sebrell[15] state that the accelerating activity of TMTD is not dependent on the presence of zinc oxide. Jarrijon suggested the addition of the TMTD molecule as dithiocarbamate radicals to the double bonds of rubber with the simultaneous formation of water and ZnDMDC. He proposed no exact mechanism but only a "statistical" reaction. He also commented with respect to the TMTD not converted to ZnDMDC, "the last one-third of the TMTD must either combine with the rubber or be decomposed, but in any event does not form TMTM". The main vulcanization reaction was postulated as a simultaneous polymerization and dehydrogenation. Both Farmer[16] and Gee[17] consider that TMTD vulcanization involves the formation of C to C linkages. Stiehler and Wakelin[18] believe that "vulcanization is not solely a cross-linking of rubber with sulfur or other primary valence bonds, but rather that both the Tuads (*i.e.*, TMTD) and metallic ion become a part of the structure of the rubber molecules".

One object of the present study was to determine what unrecognized products are formed in the vulcanizate. A survey of the literature cited seemed to indicate that new compounding data were needed to avoid unnecessary isolations and analyses on unimportant stocks. The following account of our compounding studies also includes some work suggested by the use of our various techniques to be described in the later papers of the series.

RESULTS

Role of fat acid in TMTD cures.—With respect to the effect of fat acids on TMTD cures, our results (Table I) agree with those of Jarrijon[9]. These data were obtained on compounds having the base formula A of extracted pale crepe 100, zinc oxide 5, TMTD 4, and PBNA 1.0. Recipe B had 1.5 parts of palmitic acid added.

Except for a somewhat faster curing rate and a slightly higher modulus for stock B containing the fat acid, the properties of the two stocks are similar.

Effect of variations in concentration of zinc oxide.—A series of compounds based on formula A and containing from 0 to 4 phr of zinc oxide were prepared, cured, and tested. The results are illustrated in Figure 1. From these data it appears that, for this concentration of TMTD, about 1.5 phr of zinc oxide are

TABLE I

	Recipe A				Recipe B			
Cure time at 310° F (min.)	Modulus 500%	Modulus 600%	Tensile strength	Elongation	Modulus 500%	Modulus 600%	Tensile strength	Elongation
1.5	200	350	950	675	300	550	2400	867
2.5	300	525	1800	833	375	700	3175	853
5	450	875	3400	907	550	1200	3975	803
8	550	1250	3425	800	650	1600	3550	707
11	550	1350	3850	800	600	1600	3825	717
15	625	1550	3875	740	600	1750	3800	712
23	600	1475	3250	740	575	1300	3550	705

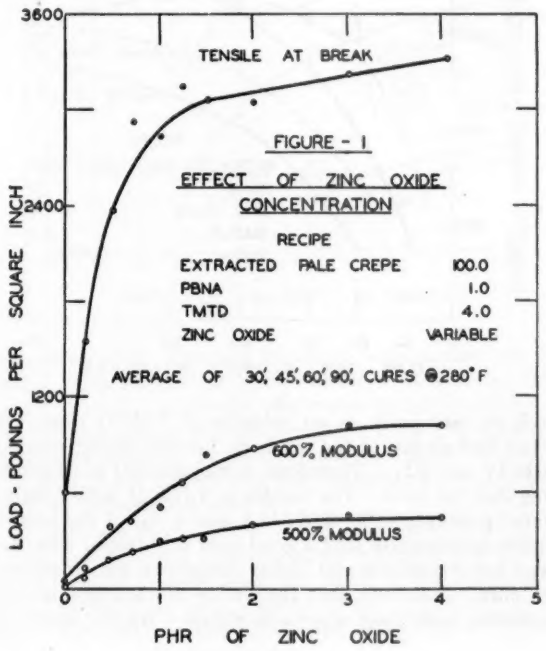
TABLE II

EFFECTS OF ZINC OXIDE AND ZINC SULFIDE
Extracted crepe 100.00—TMTD 4.00

Cure at 280° F (min.)	Zinc oxide 5.00				Zinc sulfide 5.00			
	Modulus 500%	Modulus 600%	Tensile strength	Elongation	Modulus 500%	Modulus 600%	Tensile strength	Elongation
5	—	—	—	—	50	100	700	1027
10	175	300	1900	945	175	275	2350	965
20	300	450	2750	875	250	500	3600	940
30	525	1025	3075	780	250	450	3200	925
45	575	1225	3350	733	250	350	2975	907
60	550	1225	4000	745	225	450	3200	925
90	775	1425	3450	710	200	275	2650	960
After aging 24 hours at 212° F								
45	575	1200	3100	733	200	375	2975	893
60	575	1250	2350	700	175	350	2900	875

required to develop the maximum tensile strength, while between 2.0 and 3.0 phr are required to develop maximum modulus. These data are similar to those reported by Hull, Olsen, and France[19] for mercaptobenzothiazole stocks in which the ZnO concentration was similarly varied.

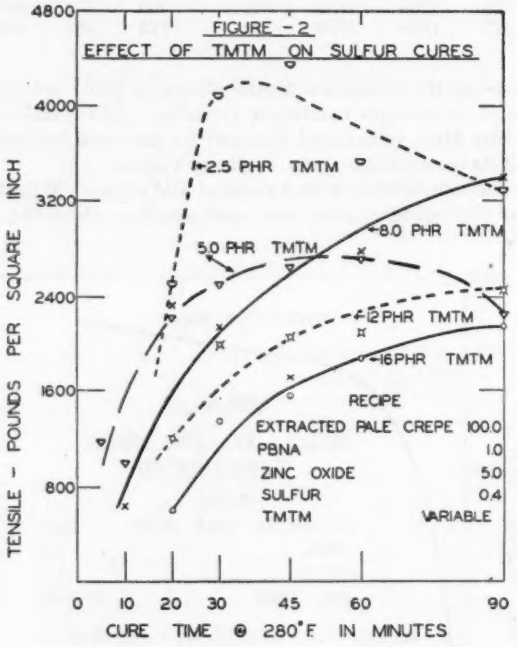
The above data show that, with 4 parts of TMTD on 100 parts of extracted rubber and no zinc oxide, a very poor cure results. However, a vulcanizate



prepared from 10 parts of TMTD and 100 of rubber was found to have the following properties which show that it was well cured:

Cure	Modulus 600%	Tensile strength	Elongation
20 min. at 280° F	250	3825	925

The vulcanizate was clear, had a strong objectionable odor, and was somewhat brittle when torn. This result definitely shows the nonessential nature of a metallic oxide for vulcanization, a fact that compounders have been aware of for a long time, although it must be admitted that certain physical properties are attributable to the presence of certain zinc compounds in the vulcanizing mixture. We have found that zinc palmitate when added in amounts up to at least 16 phr results in increased activation. The palmitate is more active on a molar basis than the oxide.

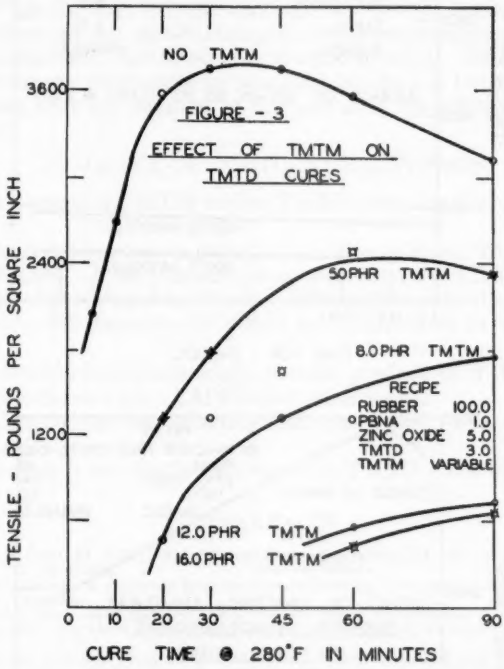


Zinc sulfide vs. zinc oxide as an activator of TMTD cures.—Bedford and Sebrell reported ZnS as one of the products formed during vulcanization (see, however, Parts IV and VI). Therefore, it was decided to determine the effect of substituting ZnS for ZnO. The results in Table II were obtained using the recipe, extracted pale crepe 100, TMTD 4, and 5 phr of the zinc compound.

These results demonstrate that a good cure is obtained with ZnS instead of ZnO but that a lower modulus and higher elongation are developed, indicating a less "tight" cure. Evidence that the ZnS is not inactive is shown by comparing these results with those shown in Figure 1 for the stock containing no ZnO.

Effect of large dosages of TMTM on vulcanization.—Since TMTD can be prepared by heating sulfur with TMTM (compare Part II) it would be reasonable to expect that, even in the presence of rubber, sulfur and TMTM would form TMTD. It may be supposed also that if excessive ratios of TMTM were used, they should have a retarding or inhibiting effect on the cure provided TMTD is incapable of vulcanization when thus stabilized.

To confirm this supposition the following two series of compounds were prepared: (1) extracted pale crepe 100, zinc oxide 5, sulfur 0.4, and TMTM 2.6, 5, 8, 12, and 16 phr; and (2) extracted pale crepe 100, zinc oxide 5, TMTD 3.00, and TMTM 0, 5, 8, 12, and 16 phr.



The stress-strain data obtained on these vulcanizates are illustrated in Figures 2 and 3. The marked inhibition observed is evidence that the above suppositions are correct. A similar effect was noted for sulfur vulcanization where ZnDMDC was used as the accelerator. A possibly related "retarding" effect of Captax and Altax on Tuads has been reported[20]. We have also found dodecanethiol to strongly inhibit TMTD vulcanization, a result which recalls Bedford and Gray's experience with H_2S.

Effect of the addition of ZnDMDC to a TMTD stock.—Since ZnDMDC is one of the principal products formed during vulcanization with TMTD and ZnO, it was of interest to determine the effect of the addition of increasing proportions of ZnDMDC to such a composition. To a base stock containing extracted pale crepe 100.0, TMTD 3.00, and ZnO 5.00, the following propor-

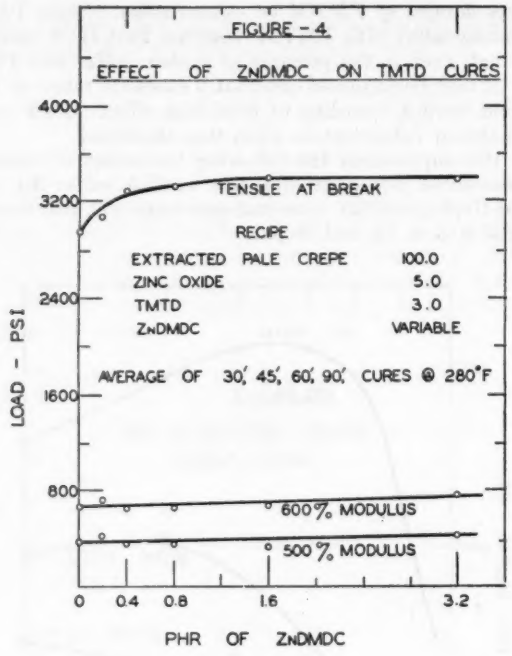
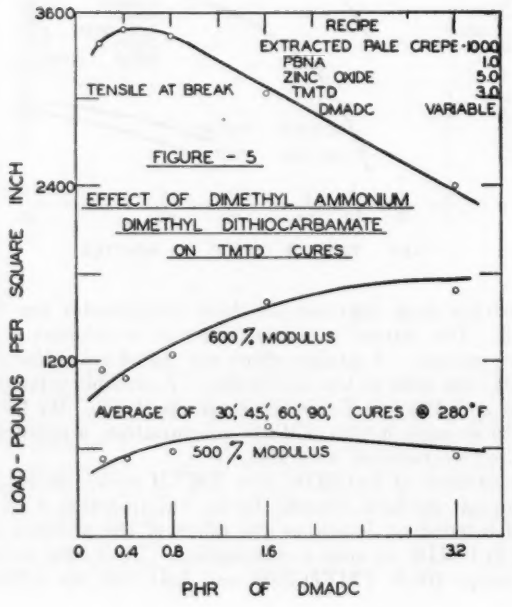


FIGURE - 4
EFFECT OF ZnDMDC ON TMTD CURES
4000
3200
2400
1600
800
LOAD - PSI
TENSILE AT BREAK
RECIPE
EXTRACTED PALE CREPE 100.0
ZINC OXIDE 5.0
TMTD 3.0
ZnDMDC VARIABLE
AVERAGE OF 30', 45', 60', 90', CURES @ 280°F
600% MODULUS
500% MODULUS
0 0.4 0.8 1.6 3.2
PHR OF ZnDMDC


3600
2400
1200
LOAD - POUNDS PER SQUARE INCH
RECIPE
EXTRACTED PALE CREPE 100.0
PBNA 1.0
ZINC OXIDE 5.0
TMTD 3.0
DMADC VARIABLE
TENSILE AT BREAK
FIGURE - 5
EFFECT OF DIMETHYL AMMONIUM DIMETHYL DITHIOCARBAMATE ON TMTD CURES
600% MODULUS
AVERAGE OF 30', 45', 60', 90', CURES @ 280°F
500% MODULUS
0 0.4 0.8 1.6 3.2
PHR OF DMADC

tions of ZnDMDC were added: 0.20, 0.40, 0.80, 1.60, and 3.20. Stress-strain data on the vulcanizates are illustrated in Figure 4. The data show that additions of the dithiocarbamate enhance the state of cure only slightly if at all. When the dithiocarbamate was tested as an activator in the absence of ZnO it was found to be about 50 per cent as effective as ZnO with respect to the maximum properties attainable, but with respect to the rate of reaction to be about the same as the oxide.

Effect of addition of dimethylammonium dimethyldithiocarbamate to a TMTD stock.—Increasing proportions of dimethylammonium dimethyldithiocarbamate[21] were added to the base stock of the preceding paragraph. The stress-strain data for the vulcanizates of the resulting mixtures are illustrated in Figure 5. While the data indicate that high ratios of the ammonium salt have an adverse effect on the tensile strength, visual examination of the vulcanizates show an increased spottiness with increasing ratios. This nonhomogeneity was undoubtedly responsible for the short breaks and low tensile strength. It is concluded that the addition of this salt does not affect the cure of the TMTD stock.

SUMMARY OF COMPOUNDING STUDIES

(1) Large dosages of TMTM inhibit TMTD vulcanization or vulcanization with sulfur.

(2) The desirability of up to about 1.5 phr zinc oxide for TMTD vulcanization was confirmed. If an unusually large amount of TMTD (10 phr) is used, a well vulcanized stock may be obtained without zinc activation.

(3) Palmitic acid displays only a mild activating effect on TMTD vulcanization.

(4) Zinc dimethyldithiocarbamate, a main product of TMTD vulcanization, is not an activator for a TMTD-zinc oxide recipe.

(5) Dimethylammonium dimethyldithiocarbamate does not activate TMTD-zinc oxide formulations.

(6) Zinc sulfide is an effective activator for TMTD vulcanization.

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Cotton and Westhead, *Trans. Inst. Rubber* **13**, 320 (1937); RUBBER CHEM. & TECHNOL. **11**, 331 (1938); Jarrijon, *Rev. gén. caoutchouc* **20**, 155, 177 (1943); RUBBER CHEM. & TECHNOL. **17**, 941 (1944); **19**, 1061 (1946); Gee, *J. Polymer Sci.* **2**, 454 (1947).

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II. STRUCTURE OF RADIOACTIVE TETRAMETHYLTHIURAM DISULFIDE

DAVID CRAIG, W. L. DAVIDSON, A. E. JUVE, AND I. G. GEIB

Tetra-substituted thiuram polysulfides are notable because of their action as "accelerators" in rubber vulcanization and also because of their ability to vulcanize rubber without added sulfur[1], especially in the presence of zinc oxide, which leads to the formation of zinc dimethyldithiocarbamate (ZnDMDC) and other substances. A study of the structure of tetramethylthiuram disulfide (TMTD) is reported in this paper. This has involved the introduction of radioactive sulfur. A corollary has been the similar study of ZnDMDC, which is an "accelerator" but not a vulcanizing agent.

The synthesis of radioactive TMTD (*i.e.*, TMTD*) was accomplished by heating 4.16 grams (0.02 mole) of tetramethylthiuram monosulfide (TMTM) and 1.28 grams (0.04 atom) of radiosulfur (S^*_8) to 120° in a stream of nitrogen for 30 minutes. By extraction with hot alcohol and benzene, a series of crystalline fractions was secured which totaled 3.38 grams, a yield of 70 per cent. This material melted at 150–156° C, with decomposition. The excess S^*_8 was recovered in a second experiment. Pyrolysis[2] of the TMTD* prepared in the above manner was carried out at 160–230° C in a modified Claisen flask. There were produced S_8*, tetramethylthiourea*, and CS_2* in nearly theoretical yield. The radioactivities of the thiuram disulfide and of the pyrolysis products (the CS_2* being converted to phenylhydrazinium phenyldithiocarbazate* or to 1-phenylthiosemicarbazide* for study), which are recorded in Table I, show that the tracer sulfur atoms distributed themselves uniformly throughout the various molecules.

We have not been able to confirm the synthesis of TMTD by the reaction between ZnDMDC and sulfur reported by Maximov[3]. Morris[4] reported that unstable addition compounds of the higher homologs of ZnDMDC and sulfur form in benzene solution. In the absence of solvent, we could observe no reaction of ZnDMDC with sulfur up to 150° C. When S_8* was in contact for 1 hour with ZnDMDC in the presence of palmitic acid at 140° C, partial consumption of the sulfur and ZnDMDC occurred. The recovered ZnDMDC was not radioactive, showing that sulfur interchange had not taken place. Palmitic acid and dimethylpalmitamide (isolated as a mixture melting at about 50° C) were identified among the products by infrared absorption and x-ray diffraction techniques. We have further found that TMTD and ZnS react to form ZnDMDC and sulfur. This behavior is essentially the reverse of the reaction reported by Maximov.

TABLE I

Substance	Expt. No.	Actual count,[b] (c/min.)	Count corr.[c] to infinite thickness (c/min.)	Theor.[d] count assuming equivalence of all S atoms in TMTD (c/min.)
Radiosulfur[a]	1	17,850	23,200	—
	2	16,250	21,100	—
TMTD	1	3590	4670	4960
	2	3600	4680	4480
Sulfur recovered from synthesis of TMTD*	1	—	—	9280
	2	7575	9850	8440
Sulfur recovered from decomposition of TMTD*	1	6570	8530	9280
	2	6975	9060	8440
Tetramethylthiourea from decomposition of TMTD*	1	1620	2110	2240
	2	1725	2240	2040
1-Phenylthiosemicarbazide	1	1325	1750	1620
Phenylhydrazinium phenyldithiocarbazate	2	1385	1800	1850

[a] Radioactive sulfur produced in Clinton Pile, Oak Ridge, Tennessee, by neutron bombardment of ordinary sulfur. This material was supplied on allocation from the Isotopes Division, U. S. Atomic Energy Commission.
[b] Count secured from a 50-mg. sample spread uniformly over a circular area of 5 sq. cm.
[c] Count corrected to that expected from a sample of infinite thickness covering the 5-sq. cm. area.
[d] Theoretical counts based on replacement of either one or two sulfurs of TMTD with S* lead to values which depart widely from the observed values.

Radiosulfur (0.01 atom), ZnDMDC (0.01 mole), and TMTD (0.0005 mole) were heated in xylene solution at 140° C for 30 minutes. The ZnDMDC isolated was found to have a radioactivity of about 22 per cent of the random radioactivity. However, when one molar equivalent of ZnDMDC and two of radio TMTD were heated in xylene solution for one hour at 120–125° C and the mixture separated, both the TMTD and ZnDMDC were found to be randomly radioactive. A random distribution of the radio-sulfur atoms was also achieved by heating equimolar amounts of radiosulfur and TMTD for 30 minutes at 120° C. [A similar result for the case of tetraethylthiuram disulfide has been reported by Mochel and Peterson[5].] The reluctance of the sulfur isotopes to interchange in the S_8*-ZnDMDC mixtures and their readiness to do so in the presence of TMTD indicates that not only may sulfur atoms undergo interchange but that the bonds to the zinc atoms may shift from one dithiocarbamate radical to another. It was found also that dimethylammonium dimethyldithiocarbamate (DMADC) in xylene solution at 140° C underwent rapid random interchange with ZnDMDC* and also with radiosulfur. Radiosulfur and CS_2 do not interchange at 140° C in xylene but when 10 per cent by weight (on the CS_2) of DMADC is also present, a slow interchange occurs. No interchange was observed when TMTD* and CS_2 were heated together at 120–125° C for 30 minutes.

The reaction of TMTD* with zinc oxide produced randomly radioactive zinc dimethyldithiocarbamate and S_8* in high yield. Also, CS_2 and CO_2 were produced here. Heating TMTD with zinc dust (reagent grade containing no ZnO) at 140° resulted in a yield of ZnDMDC which amounted to over 50 per cent. When conducted in acetone-extracted rubber in the short path still at about 130° C, this reaction produced ZnDMDC in about 60 per cent yield *as a distillate.*

The reaction of TMTD with hydrogen-supplying reagents such as dimethylamine and H_2S has been described by Delépine[6] and Bedford and Gray[7], respectively. The former reactant was reported to produce sulfur, DMADC, and tetramethylthiourea, while the latter was reported to form the same products with the sole exception that CS_2 was produced instead of the thiourea.

The reaction with dimethylamine was conducted at 100° C by Delépine. In an effort to isolate the dimethylsulfenamide suggested by the formulation:

$$(CH_3)_2NC(S)SSC(S)N(CH_3)_2 + 2\ HN(CH_3)_2 \longrightarrow (CH_3)_2NC(S)SNH_2(CH_3)_2 + (CH_3)_2NC(S)SN(CH_3)_2$$

we have operated at 50° C in benzene solution in the presence of a five-fold exesss of dimethylamine. After filtering off nearly the theoretical yield of DMADC, the filtrate was vacuum-distilled. The distillate on crystallization from hexane gave colorless crystals which melted at 50–51° C (*Calculated for* $C_6H_{12}N_2S_2$:C, 36.54; H, 7.37. *Found:* C, 36.47, 36.57; H, 7.30, 7.25). This compound when pure seemed quite stable. With impure samples, vacuum distillation caused reaction with the production of TMTD and TMTU in amounts required approximately for the following formulation:

$$3\ (CH_3)_2NC(S)SN(CH_3)_2 \longrightarrow (CH_3)_2NC(S)N(CH_3)_2 + (CH_3)_2NC(S)SSC(S)N(CH_3)_2 + (CH_3)_2N(S)N(CH_3)_2$$

The low boiling fractions reacted with CS_2 to form TMTD in agreement with the assumption that they were largely dimethylamino sulfide. We have confirmed Blake's report[8] that this substance reacts smoothly with CS_2 to form TMTD and sulfur. The dimethyl sulfenamide reacted quantitatively with CS_2 at about 110° C to form TMTD. Our results show that the sulfenamide and dimethylamino sulfide are probable intermediates in Delépine's reaction of TMTD with dimethylamine.

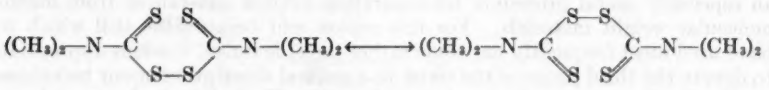
We have studied the reaction of TMTD with two new hydrogen-supplying reagents, *n*-dodecanethiol and acetic acid. The thiol yields *n*-dodecyl disulfide, CS_2, and DMADC almost quantitatively; the acid[9] yields sulfur, dimethylacetamide, CS_2, COS, and water. The dimethylacetamide has been isolated as a maximum boiling azeotrope with acetic acid. This azeotrope boils at 168° C (740 mm.) and contains about 24.5 per cent acetic acid. At the same pressure, dimethylacetamide boils at 163.5° C.

Von Braun and Stechele[10] reported that TMTM was formed by the reaction of TMTD with KCN in aqueous alcoholic solution. We have repeated this work with TMTD*, and have found the TMTM* produced to be randomly radioactive.

An obvious explanation of the above results would be that TMTD reactions proceed through the intermediary of dimethyldithiocarbamate radicals. In such radicals, the sulfur atoms become indistinguishable, and one would thus anticipate uniform distribution of radioactive sulfur atoms in the resulting products. However, the behavior of TMTD in a short-path still casts considerable doubt on this explanation. At 130–140° C and 0.001 mm. pressure, TMTD distills less readily than TMTM (mol. wt. 208). If appreciable breakdown of TMTD (mol. wt. 240) into dithiocarbamate radicals occurred at this temperature, a much greater volatility would be expected, since the molecular weight of such a radical would be 120. Ebullioscopic measurements of the molecular weight of TMTD in benzene showed that the compound actually may be polymerized in this solvent. The molecular weight, extrapolated to infinite dilu-

tion, was found to be 235 and in a 5.4 per cent solution to be 257 ± 2. This, together with the distillation behavior, is additional evidence against the assumption that appreciable dissociation takes place.

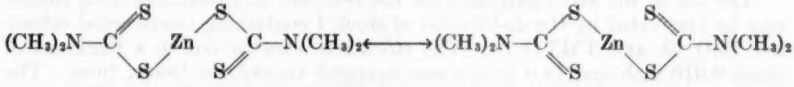
It appears to us that the conflicting evidence cited above can be satisfactorily resolved if we assume that the TMTD molecule contains a planar six-membered ring and is viewed as a hybrid of two identical contributing forms as follows:



This hybrid should be sufficiently susceptible to initial attack to account for the products which have been observed, and the equivalence of the sulfur atoms comprising this structure would adequately explain the random distribution of the radioactive sulfur. The weakest part of the hybrid ring would be expected to be the S—S bonds. Opening of these to form a diradical would give an intermediate capable of polymerization as shown by the ebullioscopic results, or of reaction with the various reagents including ZnDMDC which have been tested. On this basis, it becomes unnecessary to postulate dissociation of the TMTD as an initial step and thus we are able to account for the observed reluctance to distill at low pressures.

After this paper was written several important publications on TMTD appeared. Thus, Koch[11] reported on the ultraviolet absorption of TMTD and on its other properties. His ideas of TMTD structure are similar to ours. He reported that solutions of TMTD on heating developed a color which disappeared on cooling and accepted this behavior as evidence for dissociation into dithiocarbamate radicals. Another view which is consistent with the observations and interpretations presented in this set of papers and elsewhere is that TMTD, which is colorless, dissociates reversibly into TMTM, sulfur, and polysulfides, all of which are colored. The "thermochromasy" of TMTD and some other properties of interest to its vulcanizing action were discussed by Bergen[12].

The fact that ZnDMDC (mol. wt. 305) can be short-path distilled, though somewhat less readily than TMTD, lends support to the structure proposed, since ZnDMDC can also be written as a six-membered ring hybrid with the zinc atom in the center of the ring as follows:



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III. SHORT-PATH DISTILLATION OF TMTD AND ITS REACTION PRODUCTS FROM RUBBER

DAVID CRAIG, A. E. JUVE, AND W. L. DAVIDSON

During the course of this study we have found short-path distillation to be an especially useful procedure for separating volatile substances from macromolecular weight materials. For this reason and because the still which we have used most frequently has some rather novel features, it seems appropriate to devote the third paper of the series to a general description of our technique.

Figure 1 is a schematic drawing of the still. Tube A is the heater tube, to the outside of which the samples in sheeted out form are attached by means of copper wire. The heater tube contains about 30 cc. of a liquid whose boiling point is the temperature at which the distillation is to be conducted. The liquid is boiled by an internal heating element regulated by means of a variable transformer. The leads H to the heating element enter through a rubber stopper in the upper end of the heater tube which is open to the atmosphere through flask G. For low-boiling heater liquids such as methanol, a condenser must be attached to the upper end of the heater tube. For the work described in the present series of papers, Cellosolve, b.p. 133° C, was used as the heater liquid.

Tube B of Figure 1 is the condenser tube. Ordinarily, air cooling is sufficient to condense such materials as the usual rubber antioxidants, softeners, accelerators, fat acids, sulfur, etc. For special purposes, tube B is cooled by wrapping it with rubber tubing through which tap water was circulated or it is cooled with dry ice. The gap of this still, *i.e.*, the distance from the heater tube to the condenser tube, is about 2 cm.

The U-tube C, made of 1.25-inch glass tubing, constitutes a trap. It usually has been cooled with dry ice and acetone in I. That U-tube is connected to a booster pump[1] D through a second dry-Ice trap. The pressure usually used has been less than 0.01 mm. and has been measured by a McCleod gage attached to E below the dry ice trap F. Where higher pressures have been used, the vacuum source has usually not included the booster pump.

DISTILLATION OF SOME UNEXTRACTED RUBBER STOCKS

The use of the short-path still for the recovery of substances from rubber may be illustrated by the distillation of stock I containing unextracted rubber 100, ZnO 10, and TMTD 10. The stock was sheeted out to a thickness of about 0.010 inch and 18.0 grams was wrapped around the heater tube. The still was evacuated and the heater started. After liquid (b.p. 133°) had refluxed to the top of the heater tube, the still was operated for four hours, during which time the pressure fell from 0.015 to 0.006 mm. The still was allowed to cool before opening to the atmosphere. The condensate on the inside of the condenser tube was rinsed into a tared 250-cc. beaker with benzene, using a transfer pipet with rubber bulb attached. Evaporation of the benzene in a nitrogen stream left a residue of 1.6 grams, from which 1.15 grams TMTD, m.p. 143–150°, was isolated. Thus, 77 per cent of the TMTD added to the stock was recovered. The stock removed from the heater tube weighed 16.4 grams. It was slightly cured. The rate of distillation of the TMTD, thus, was greater than its rate of reaction in the rubber.

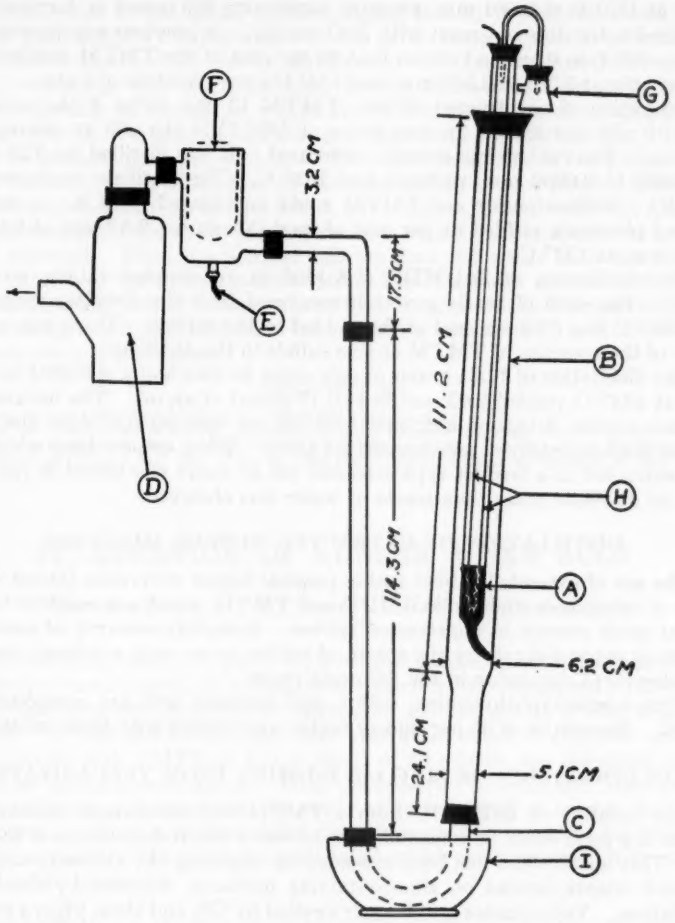

FIG. 1.

A second experiment with 18.00 grams of stock I was conducted. In this case the still was operated at atmospheric pressure for two hours. The gases, CS_2, $(CH_3)_2N—H$, CO_2, H_2S, H_2O, and $(CH_3)_2NC(S)N(CH_3)_2$, evolved during the period were discarded. A vacuum was then applied for 2.75 hours. The distillate was removed as before, except that it was necessary to use a "policeman" on the end of a long rod to loosen the part which did not dissolve in the solvent. No TMTD could be detected in the distillate, but 0.4 gram Zn-DMDC and 0.11 gram TMTM were isolated. Dimethylammonium dimethyldithiocarbamate was isolated in small amount. The rubber was tightly cured. It weighed 16.9 grams.

A stock consisting of unextracted rubber 100, TMTM 10, and zinc oxide 10, yielded 90 per cent of the TMTM as distillate, n.p. 103–107° C, during 3.5

hours at 133° C at 0.001 mm. pressure, confirming the report of Jarrijon[2] that this accelerator does not react with ZnO readily. A previous experiment with a zinc oxide-free stock had shown that 86 per cent of the TMTM distilled during one hour at 0.001 to 0.010 mm. and 133° C from a mixture of 3 phr.

A mixture of unextracted rubber, TMTM 10 phr, sulfur 3 phr, and zinc oxide 10 phr was heated for two hours at 133° C in the still at atmospheric pressure. The rubber was severely overcured. It was distilled for 3.25 hours at 0.0004 to 0.0002 mm. pressure and 133° C. The distillate contained ZnDMDC. Neither sulfur nor TMTM could be isolated from it. A rubber-sulfur 3 phr stock yielded 91 per cent of its sulfur during 2.5 hours at 0.001 to 0.010 mm. at 133° C.

The distillation of ZnDMDC (1.8 phr) in unextracted rubber was also tested. The yield of nearly pure salt recovered from the distillate melting at 243–245° C was 62.5 per cent of that added to the rubber. There was no evidence of the presence of TMTM or zinc sulfide in the distillate.

The distillation of 11.34 grams of pale crepe for two hours at 0.0004 to 0.001 mm. at 133° C yielded 2.02 per cent (0.17 gram) of an oil. The infrared absorption curves of this oil and oleic acid (98 per cent purity) show the oil to consist predominantly of unsaturated fat acids. When crepe rubber which had been extracted in a Soxhlet type extractor for 48 hours was tested in the same way, no distillate other than traces of water was observed.

DISTILLATION OF EXTRACTED RUBBER MIXTURES

The use of extracted rubber makes possible higher recoveries (about 90 per cent) of substances such as ZnDMDC and TMTD, which are reactive toward the fat acids present in unextracted rubber. Complete recovery of such substances is made difficult by the action of rubber as an acid, a subject reserved for subsequent discussion in the following paper.

Phenyl-beta-naphthylamine, sulfur, and palmitic acid are completely removed. Recoveries of 95 per cent or higher are feasible with these substances.

VOLATILIZATION OF ZINC (AS ZnDMDC) FROM VULCANIZATES

The isolation of ZnDMDC from a TMTD-ZnO vulcanizate showed that zinc in this form could be removed from rubber without destruction of the rubber. This observation has been extended by studying the alternate action of CS_2 and dimethylamine on zinc-containing mixtures, followed by short-path distillation. Vulcanizates are strongly swelled by CS_2 and then, when a swollen sample is submerged in a 25 per cent dimethylamine solution, ZnDMDC[3] and dimethylammonium dimethyldithiocarbamate are precipitated in the rubber. Both of these salts can be short-path distilled from rubber.

An example is the procedure applied to stock II consisting of extracted rubber 100, ZnO 5.00, and TMTD 4.00, cured 45 minutes at 280° F. After short-path distillation to remove the low molecular weight products of vulcanization, it was found to contain 3.23 per cent zinc, 0.45 per cent total sulfur, and 0.17 per cent "zinc-sulfide" sulfur. It did not show an *x*-ray diffraction pattern for zinc sulfide. A 1.900-gram sample (0.025 inch thick) was swollen to about seven times its size in CS_2 and then submerged in 25 per cent dimethylamine solution for three hours. Short-path distillation at 0.3 mm. at 133° C removed water, dimethylamine, and dimethylammonium dimethyldithiocarbamate, but almost no ZnDMDC. At 0.0005 mm., however, 0.070 gram of ZnDMDC distilled during two hours at 133°. The sample was turned over on the heater

and 0.045 gram. of ZnDMDC distilled during two hours at 0.0005 mm. The sample then weighed 1.835 grams. It was given a second treatment with CS_2 and dimethylamine, followed by distillation. It then weighed 1.805 grams. A third treatment with CS_2 and dimethylamine, followed by short-path distillation, resulted in no change in weight and in the formation of no ZnDMDC. The sample was transparent and still in a high state of vulcanization. It was found to contain 0.03 per cent Zn. This remaining zinc is evidently quite firmly bound. While zinc added in the form of ZnO or zinc palmitate may be removed satisfactorily by the treatment, nevertheless, if combined with a strong nonvolatile acid, it then may not be removed. Also, ZnS compounded as such is not removed. Thus, the residual 0.03 per cent of Zn may be in the form of ZnS. Since the vulcanized sample before the treatment contained 0.17 per cent "zinc sulfide" sulfur (that removed by ether and HCl[4]), it is apparent that two forms of this sulfur may have been present, one of which is labile toward the zinc removal treatment.

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IV. BEHAVIOR OF RUBBER AS AN ACID

DAVID CRAIG, A. E. JUVE, AND W. L. DAVIDSON

The retarding effect of organic acids on vulcanization as well as the activating effect of certain acids on certain accelerators is well recognized. The activating and accelerating effects of bases and metallic oxides is also well recognized. In this connection, the mild activating effect of palmitic acid on vulcanization with TMTD in the presence of zinc oxide was described in the first paper of the present series. With the behavior of acids and bases during vulcanization as a background, the study of rubber itself as an acid has been undertaken. This paper sets forth a description of two reactions investigated during the study. These are the reaction of rubber with zinc palmitate and of TMTD with acids.

REACTION OF EXTRACTED RUBBER WITH ZINC PALMITATE

The short-path still technique of Part III is well suited to the study of this reaction, which forms palmitic acid and apparently a zinc salt of rubber. When varying amounts of the zinc palmitate were milled on a warm mill into extracted crepe containing 1 phr of phenyl-beta-naphthylamine and the resulting clear mixtures (40 grams of each) were short-path distilled, the amount of palmitic acid liberated approached a limiting value of about 1.0 phr as the amount of zinc palmitate added to the rubber was increased. The results are plotted in Figure 1. The equivalent weight of rubber calculated from 1.0 phr (0.0039 equivalent) of palmitic acid is 25,700. An idea of the efficiency with which zinc palmitate reacts with rubber may be had by noting that 0.0039 equivalent equals 1.12 grams of zinc palmitate. According to Figure 1, the yield of palmitic acid resulting from mixing this amount of zinc salt into rubber is 0.56 phr or 56 per cent. To drive the reaction to completion, that is, to

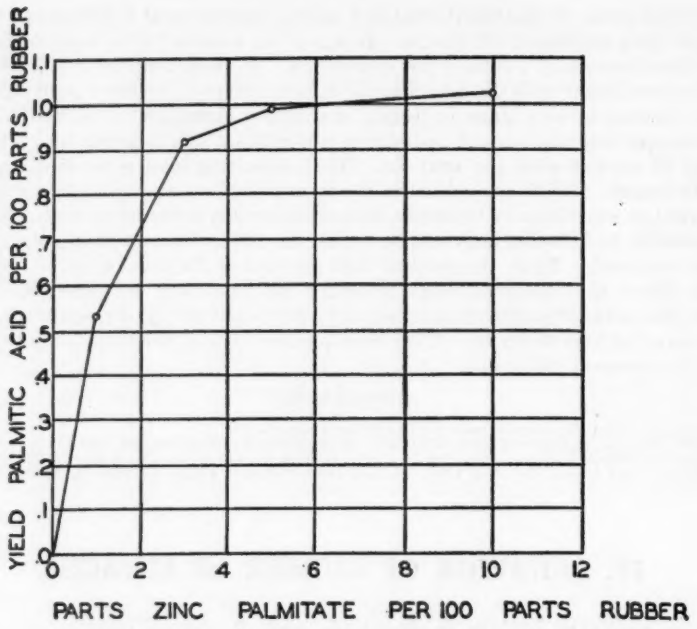

FIG. 1.—Palmitic acid recovered by distillation of rubber-zinc palmitate mixtures.

realize a recovery of palmitic acid equivalent to the acid groups in the rubber, about 5 phr of zinc palmitate must be added to the rubber.

This reaction can be understood on the basis of reaction I, followed by re-

$$RC(O)OH + Zn(OC(O)C_{15}H_{31})_2 \rightleftharpoons HOC(O)C_{15}H_{31} + RC(O)OZnOC(O)C_{15}H_{31} \quad (I)$$

action II. Here, R is the portion of the rubber molecule attached to a single acid group which is assumed to be C(O)OH. In the presence of excess zinc palmitate, reaction I can go to completion to the right and reaction II is repressed. When the palmitic acid is allowed to volatilize in the short-path still,

$$RC(O)OZnOC(O)C_{15}H_{31} + RC(O)OH \rightleftharpoons RC(O)OZnOC(O)R + HOC(O)C_{15}H_{31} \quad (II)$$

both reactions shift to the right. Reaction II requires that two acid groups be sufficiently near each other. With a macromolecular weight acid such as rubber, it would seem that this condition would not always be met. If this condition does not exist, the probability of the existence of the mixed salt formed by reaction I is increased and the probability of a "zinc salt cross-link" is decreased.

The reaction of rubber (a hydrophilic substance) with zinc palmitate was at first thought to involve only hydrolysis (reaction III) of the salt of a weak acid

$$Zn(OC(O)C_{15}H_{31})_2 + HOH \rightleftharpoons Zn(OH)OC(O)C_{15}H_{31} + HOC(O)C_{15}H_{31} \quad (III)$$

and a weak base. Doubt was cast on this view when it was found that zinc palmitate could be recrystallized from a boiling mixture of toluene and water

with nearly quantitative recovery of the salt, m.p. 131–132° C. That hydrolysis is involved in the formation of palmitic acid in a rubber stock (originally containing 1.5 phr of zinc palmitate), however, was shown by remilling it after short-path distillation. Water was absorbed from the atmosphere, even on a warm mill, and then, when the stock was again short-path distilled, a further amount of palmitic acid was collected. The first distillation produced 0.92 phr and the second 0.04 phr, a total of 0.96 phr. This is nearly the limiting amount of 1.0 phr of palmitic acid. In another experiment 4.6 phr of zinc palmitate was compounded. After short-path distillation, the stock was placed over water in a humidifier for three days. During this period it increased in weight by about 1 per cent. When it was short-path distilled, the total yield of palmitic acid from both distillations amounted to 2.93 phr.

The possibility of reactions (reactions IV and V) of the zinc salts produced

$$RC(O)OZnOC(O)C_{15}H_{31} + HOH \rightleftharpoons HOC(O)C_{15}H_{31} + RC(O)OZn - OH \quad (IV)$$

$$RC(O)OZnOC(O)R + HOH \rightleftharpoons RC(O)OZnOH + RC(O)OH \quad (V)$$

by reactions I and II with water should also be considered. The products RC(O)OZnOH formed in these reactions would not be stable in the presence of excess zinc palmitate in the short-path still because reaction VI would occur. The products of reactions VI and I are identical. The palmitic acid liberated

$$RC(O)OZnOH + Zn(OC(O)C_{15}H_{31})_2 \longrightarrow RC(O)OZnOC(O)C_{15}H_{31} + HOC(O)C_{15}H_{31} \quad (VI)$$

by I, II, III, IV, and VI should repress the hydrolytic reactions, however, while the nonvolatile rubber acid RC(O)OH tends to release water (reaction V), which can either volatilize or enter into reactions III, IV, and V. Only when large amounts of both zinc palmitate and water are present would reaction III seem to be important.

A reaction bearing on the hydrolysis of zinc palmitate is the synthesis of the zinc salt from zinc oxide and palmitic acid. It was at first postulated that the reaction would be aided by reduction of the pressure. However, at 0.2 mm. pressure, equivalent amounts of reagent grade zinc oxide and palmitic acid did not react completely at 160° C during two hours. When 0.815 gram (0.01 mole) of ZnO, 5.37 grams (0.021 mole) of palmitic acid, 30 cc. of toluene and 5 cc. of water were refluxed at 94° C for 40 minutes, a transparent two-phase liquid system was obtained. The mixture was cooled to room temperature and the colorless crystals which formed were filtered with suction and washed with 20 cc. of benzene. The yield of air-dried zinc palmitate melting at 129–131° C amounted to 5.595 grams or 97 per cent. An experiment differing from the one described in that the water was omitted and also in that 20 cc. of benzene was added to get refluxing at 95° C was next conducted. The starting materials were recovered quantitatively. Whitmore and Lauro[1] reported that zinc palmitate prepared from sodium palmitate and zinc acetate melted at 129° C, but gave no analytical data. Our product recrystallized from toluene melted at 133° C, and was found to contain 11.34 per cent of zinc, which is the calculated value for $Zn(OC(O)C_{15}H_{31})_2$.

The possible reaction of zinc oxide with palmitic acid in extracted rubber during milling was examined briefly. The stock used was rubber 100, ZnO 6.25, and palmitic acid 2.00. When mixed at room temperature and then short-path distilled for one hour at 133° C at 0.0007 mm., 89.4 per cent recovery of the palmitic acid was realized. The same stock, except that excess water was

added before sheeting off the mill was distilled in the same way. The recovery of palmitic acid amounted to 93.4 per cent. Little reaction appeared to have occurred, wet or dry, during the mixing.

The reaction of zinc oxide with palmitic acid is thus seen to be inhibited by a moderate degree of desiccation and to fail to occur even in wet rubber on the mill. It would be classified by Smith[2] as ionic in nature and, therefore, requiring a dissociating medium. It is interesting to note that zinc oxide, zinc palmitate, and palmitic acid are not water-soluble and do not absorb water in more than small amounts. The reaction of zinc palmitate with rubber is also ionic in nature, and whether or not water is necessary, it has always been present. The effects of water on the yield of palmitic acid from zinc palmitate-rubber mixtures are difficult to evaluate because these substances codistill from rubber in the short-path still. However, the experiments described show that rubber *at least in the presence of water* acts as an acid toward zinc plamitate. It may not be amiss to point out that water acts as an acid in the hydrolysis of any salt. Thus, rubber could be acting merely as a solvent for the hydrolysis. Independent evidence that rubber is an OH acid is supplied by a comparison of the reaction of fat acids with TMTD, which forms dimethylamides, and the reaction of rubber with TMTD. These reactions are discussed in the following section.

The palmitic acid values of Figure 1 were determined by titration of the short-path distillates. Palmitic acid recovered in similar experiments from phenyl-beta-naphthylamine-free stocks has been found to melt at 62–63° C. In such cases the acid is usually determined by weighing. Figure 1 seems to be reproducible to within about 10 per cent from one batch of rubber to another. The rubber removed from the short-path still containing the zinc salts of rubber and zinc palmitate was tacky. It lost a part of this tackiness by being allowed to absorb mositure. Crystallization (blooming) did not take place on long standing of the stocks containing up to 5 phr of zinc palmitate.

FORMATION OF DIMETHYLAMIDES FROM TMTD

Dimethylamide formation from TMTD, a new reaction, was first investigated with palmitic acid. Equimolecular amounts of this acid and TMTD were heated for 30 minutes at 130–140° C. By crystallization of the reaction mixture from alcohol, 80 per cent recovery of the TMTD was secured. Longer periods of heating were found to produce dimethylpalmitamide, sulfur, and CS_2.

The reaction of 48 grams (0.2 mole) of TMTD with 60 grams (1 mole) of acetic acid was conducted for five hours at 125° C. The products which distilled during this period included water, CS_2, COS, and a small amount of H_2S. Sulfur separated from the reaction mixture on cooling to room temperature. The mixture was filtered to supply a yield of 6.01 grams of sulfur or 94 per cent of the amount calculated from the reaction:

$$[(CH_3)_2NC(S)S]_2 + 2\ HOC(O)CH_3 \longrightarrow H_2O + CS_2 + COS + 2\ (CH_3)_2NC(O)CH_3 + (S)$$

The distillation at 10 mm. of the filtrate provided a series of fractions, the lowest boiling one being recovered acetic acid. The higher boiling fractions were refractionated at atmospheric pressure to give a main fraction distilling at 167–169° C at 740 mm. This fraction contained 23.5 per cent acetic acid, as shown by its titration with sodium hydroxide. Pure dimethylacetamide (b.p. 163.5°

C, 740 mm., m.p. −19°) and acetic acid were found to form a maximum boiling mixture containing 24.5 per cent acetic acid, which distilled at 168° C at 740 mm. Based on the titration of the acetic acidimethylacetamide fractions and their weights, the dimethylacetamide yield amounted to 35 grams or 0.40 mole. This is the theoretical yield based on the above equation. That acetic acid was present in the 167–169° C boiling fraction was shown by its piperazine hydrate derivative, which we have found to melt at 235–240° C, with decomposition. Addition of the derivative which melted at the same temperature and which was prepared from an authentic specimen of acetic acid produced no change in the melting point. The value given in the literature[3] for this derivative, 208.5–209° C, we believe to be in error.

The reaction of equimolecular amounts of TMTD with acetic anhydride at 140–145° C during five hours formed the following substances: sulfur (74%), dimethylacetamide (93.5%), COS (68%), CS_2 (110%), and small amounts of tetramethylthiourea. The percentages given are based on the equation:

$$[(CH_3)_2NC(S)S]_2 + [CH_3C(O)]_2O \longrightarrow (S) + 2\,(CH_3)_2HC(O)CH_3 + COS + CS_2$$

The yield of CS_2 of over 100 per cent, the formation of tetramethylthiourea, and the recovery of about 6.5 per cent of the acetic anhydride started with, show that this is not the only reaction that occurred, though it is the main one.

Since TMTM is a reaction product of TMTD vulcanization in the presence of zinc oxide, a mixture of 0.01 mole TMTM, 0.01 atom sulfur, 0.02 mole of palmitic acid, and 0.01 mole of ZnO was heated for two hours at 1 mm. to 0.3 mm. pressure. The products which were separated and identified included ZnDMDC, zinc palmitate, dimethylammonium dimethyldithiocarbamate, and dimethylpalmitamide. About one-third of the sulfur and one-half of the ZnO remained. No ZnS could be detected. The TMTM and palmitic acid were almost completely consumed. This reaction is similar to the reaction of palmitic acid, TMTD, and zinc oxide which, therefore, will not be described.

The formation of dimethylpalmitamide in an extracted rubber-zinc palmitate (10 phr) stock was demonstrated by an experiment that will be described in some datail. As a preliminary step this stock was short-path distilled to remove palmitic acid. Then 5 phr of zinc oxide and 4 phr of TMTD were added on the mill. A 42.5-gram sample 0.010 inch thick was cured in the short-path still at atmospheric pressure for 1.5 hours at 133° C. The distillate amounted to 0.235 gram, from which 0.05 gram of TMTD was recovered by crystallization from hexane. Gaseous products were not identified. The rubber was severely overcured. It was left in place in the still and distilled for two hours at 0.001 to 0.0005 mm. The distillate, amounting to 1.09 grams, was removed and distillation conducted for a second period of 2.5 hours. The distillate (total = 1.42 grams) was separated into alcohol-soluble and alcohol-insoluble fractions. One of the insoluble fractions weighed 1.09 grams, and melted at 238–243° C. A second insoluble fraction melted at 130–240° C and weighed 0.22 gram. These fractions were identified by x-ray diffraction studies. The patterns are shown in Figure 2 along with the patterns for ZnDMDC and zinc palmitate. The diagrams for the two fractions correspond to superpositions of the patterns for the two pure substances. A study of the patterns for artificial mixtures of the two pure substances permits us to say that the high melting fraction is about 80 per cent ZnDMDC, while the 130–240° C melting sample is about 20 per cent ZnDMDC. Since zinc palmitate is nonvolatile, its appearance in the distillate is without doubt due to the reaction of palmitic acid with ZnDMDC after these substances have distilled from the vulcanizate.

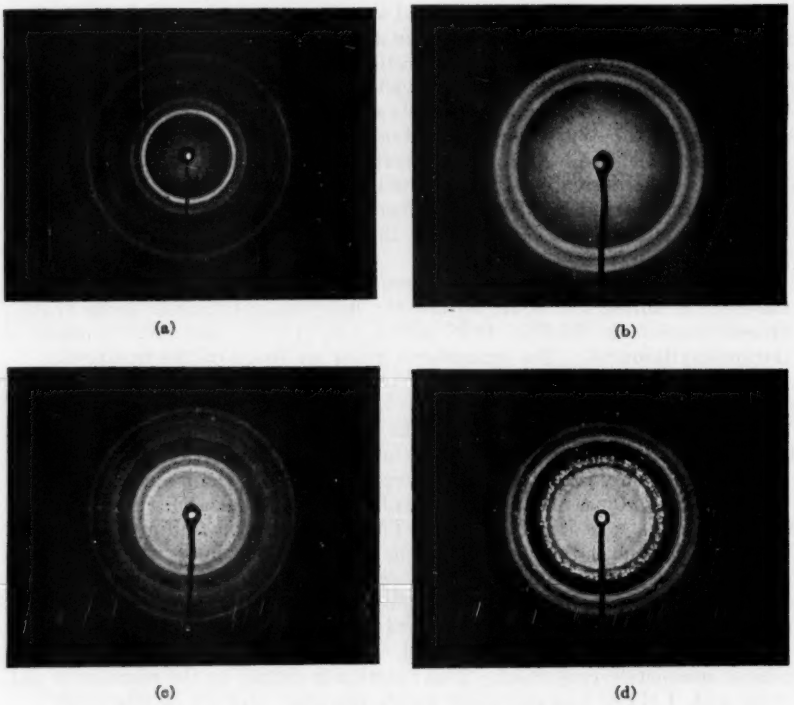

FIG. 2.—(*a*) Zn DMDC; (*b*) zinc palmitate; (*c*) specimen melting 238–243° C; and (*d*) specimen melting 130–240° C. All patterns made utilizing CuK x-radiation. Sample-film distance 5 cm.

The presence of dimethylpalmitamide as a double compound with palmitic acid in the alcohol-soluble fraction was established by infrared absorption, *x*-ray diffraction, and melting point techniques. The alcohol-soluble fraction also contained TMTM.

The formation of dimethylamides as just described suggests that, if rubber is an OH acid, it too should react with TMTD to form a dimethylamide. The nitrogen analysis of extracted crepe rubber before and after vulcanization with 4 phr of TMTD and 5 of ZnO is given in Table I. The cured stock was short-path distilled to remove ZnDMDC before analysis. The difference between the nitrogen content before and after vulcanization amounts to 0.053 per cent, or to 0.0038 equivalent phr. This value checks the 0.0039 equivalent of palmitic acid liberated from zinc palmitate in the short-path still, and thus confirms the presence of an OH acid group in rubber.

TABLE I

Sample	Extracted crepe % N	Vulcanizate % N
Sample A	0.388	0.439
Sample B	0.386	0.441
Average	*0.387*	*0.440*

A correlation of the zinc removal study of the preceding paper with dimethylamide formation also supports the conclusion that rubber is an OH acid. The vulcanizate just described was one used in the zinc removal study. Before the zinc removal treatment, it was found to contain 0.17 per cent "ZnS" sulfur and 3.23 per cent zinc. After the treatment it was not analyzed for sulfur, but the zinc content was found to be 0.03 per cent, equivalent to 0.015 per cent zinc sulfide sulfur. Since the zinc removal treatment does not remove ZnS added as such, we feel that most of the 0.17 per cent "ZnS" sulfur in reality may be a zinc hydrosulfide or a more than usual reactive form of zinc sulfide in which at least one valence of the zinc atom is bound to carbon through sulfur or oxygen. It should be emphasized that the low zinc content of 0.03 per cent is to be expected if rubber contains —C(O)OH groups, which by the action of TMTD are converted to dimethylamide groups. If the acid groups of the rubber molecule are not hydroxylic, the treated stock should contain 0.0039 equivalent of zinc phr, or 0.125 phr of Zn.

The acid equivalent of crepe rubber of 25,700, based on the liberation of 0.0039 equivalent of palmitic acid phr from zinc palmitate, permits the calculation of the oxygen content of the rubber as 0.125 per cent if we assume that the acid group is —C(O)OH and that no other oxygen containing group is present. This result is in agreement with the "general average" value of 0.13 per cent calculated by Wing[4] from the carbon and hydrogen analyses of purified rubber. The correlation of the acid equivalent with Wing's figures is, of course, nonexistent if the view is taken that the 0.13 per cent value represents impurity oxygen.

The extent to which rubber is acidic, as shown by the experiments described here, is slight and appears to disclose nothing about the nature of the vulcanization process.

Midgley and others[5] investigated the reaction of rubber with organic metallic compounds, including thienyl Grignard reagents. These reagents failed to form a sulfur-containing reaction product, and therefore it was concluded that rubber is neither ketonic nor carboxylic. The reversible vulcanization effects noted by these authors, however, are compatible with the liberation of palmitic acid by the reaction of rubber with zinc palmitate.

[1] Whitmore and Lauro, *Ind. Eng. Chem.* **22**, 646 (1930). See also Jacobsen and Gardner, *Ind. Eng. Chem.* 33, 1254 (1941).
[2] Smith, "Effects of Moisture on Physical and Chemical Changes," Longmans Green, New York, 1929, p. 145.
[3] Pollard, *et al.*, *J. Am. Chem. Soc.* **56**, 1759 (1934).
[4] Wing, *Science* **105**, 363 (1947).
[5] Midgley, Henne and Shepard, *J. Am. Chem. Soc.* **56**, 1156 (1934); Midgley, Henne, Shepard, and Renoll, *J. Am. Chem. Soc.* **57**, 2318 (1935).

V. LOW MOLECULAR PRODUCTS AND THE MECHANISM OF ZINC OXIDE ACTIVATION

DAVID CRAIG, W. L. DAVIDSON, AND A. E. JUVE

The essential features of TMTD vulcanization, as revealed by compounding studies, were discussed in Part I of this series. Thus, TMTM, a product of TMTD vulcanization, and an active accelerator of sulfur vulcanization, was found to be an inhibitor, and ZnDMDC, a main product of TMTD vulcanization, in the presence of ZnO was found to be devoid of activating properties.

As a replacement of ZnO, which is a potent activator, ZnDMDC displayed only mild activating effects. Zinc palmitate was even more potent than ZnO. Zinc sulfide was somewhat less active than ZnO. Palmitic acid and DMADC had little or no effect on the cure. The second paper reported that TMTD could be prepared in good yield by the reaction of TMTM with sulfur and also, as a result of radiosulfur techniques, that the four sulfur atoms in the TMTD molecule are chemically identical. Part II also reported that ZnO reacted with TMTD to form sulfur and ZnDMDC in good yield. Other reactions of TMTD were discussed. Part III, in presenting a short-path distillation technique for studying vulcanizates, reported that the nearly complete removal of zinc from the TMTD vulcanizate is not accompanied by devulcanization. Part IV reported on the behavior of rubber as an acid. This behavior results in the liberation of palmitic acid from zinc palmitate. From the comparison of the reaction of TMTD with acids and the reaction of rubber with TMTD, it was inferred that rubber is an OH-containing acid. Acids in the work reported were found to react rather slowly with TMTD to form dimethylamides and sulfur in good yield. The acidic nature of rubber did not seem to be great enough to contribute in any fundamental way to the vulcanization process.

The present paper describes further studies of the TMTD vulcanization problem.

RADIOACTIVE TMTD PRESS VULCANIZATION

The stock used in one experiment consisted of extracted crepe 100, radioactive TMTD 4.00, and ZnO 5.00. Four sheets (15.285 grams 2.25 × 4.25 × 0.025 inches) were press-cured for 45 minutes at 280° F. Then they were subjected to short-path distillation at 0.3 mm. for 4.5 hours. The distillate which had collected during this time was separated into TNTU (0.025 gram), TMTM (0.045 gram) and ZnDMDC (0.275 gram, m.p. 246–248° C). A further period of distillation for 5.5 hours at 0.001 to 0.0002 mm. yielded 0.115 gram of nearly pure ZnDMDC, which melted at 237–240° C.

Table I constitutes a summary of the experiment and includes the weights and radioactivities of the starting materials and of the products. The activity[1] of the S_8* used in making the radioactive TMTD is included in Table I. Start-

TABLE I

Sample	Weight(g.)	Moles	Radioactivity of 5-cm.² area sample corrected to infinite thickness (c/m)	Theoretical count assuming random distribution of S (c/m)
1. Radiosulfur	—	—	22,150	—
2. Radio TMTD used in compound	0.561	0.00234	6,350	6740
3. Stock before distillation	15.285	—	147	—
4. Stock after distillation	14.765	—	38	53.7
5. Total material distilled from stock	0.520	—	—	—
6. TMTM isolated	0.045	0.00022	5,700	5500
7. TMTU isolated	0.025	0.0001	2,530	2880
8. ZnDMDC, m.p. 246–248° C	0.275	—	5,630	5000
ZnDMDC, m.p. 237–240° C	0.115	0.00128	—	—
9. "ZnS" sulfur by analysis	0.0252	0.000786	—	—
10. Organic sulfur by analysis (total S — "ZnS" S)	0.0414	0.00129	—	—

ing with this sulfur (4 atoms) having an activity of 22,150 counts per minute and TMTM (1 mole), the calculated random activity of the TMTD equals $22{,}150 \times 4/7 \times 53.3\% = 6740$ c/m since TMTD contains 53.3 per cent sulfur, and since the reaction involves the intermingling of the three sulfur atoms in the TMTM molecule with the four starting sulfur atoms. The final two columns of the table present the radioactivity data compiled in the course of the experiment. Column 4 contains the experimental counts deduced for a sample 5 sq. cm. in area and of thickness greater than the maximum range of S^{35} beta-rays. Column 5 lists the theoretical counts that would be expected on the assumption that the four sulfur atoms in the TMTD molecule are chemically equivalent and distribute themselves equally in the resulting products.

The vulcanizate after distillation was found to contain 0.45 per cent total sulfur. Based on the sulfur content, the calculated random activity of the distilled stock is 53.7 c/m. The found value is in fair agreement if the 60 c/m background of our counter is taken into consideration. The experimental activities of the stock and the other substances check the theoretical values sufficiently well to lead to the conclusion that the isotopic sulfur atoms of the TMTD molecules distributed themselves uniformly among the products. The organic sulfur of the distilled vulcanizate (see column 3 in Table I) amounted to 0.00129 mole or to 0.55 atom of sulfur per mole of TMTD compounded. This value is not in agreement with the usual idea that one atom of sulfur in the TMTD molecule is available for vulcanization in the presence of ZnO. If the "ZnS" sulfur is included with the organic sulfur as an essential part of the vulcanizate, then 0.89 atom of the four TMTD sulfur atoms may be considered to have become "available."

TABLE II

Treatment	Tensile strength (lb. per sq. in.)	Elongation (%)	Zn (%)	"ZnS" S	Organic S
After vulcanizing 45 min. at 280° F	3300	775	1.5	—	—
After short-path distillation of above stock	3500	760	0.94	0.03	0.36
After one Zn removal treatment	3500	780	0.14	0.000	0.35
After two Zn removal treatments	3600	760	0.017	—	—

There seems to be no reason for considering the "ZnS" sulfur any more essential than the ZnDMDC sulfur which was distilled from the vulcanizate. Moreover, in the third paper, it was shown that nearly all the "ZnS" sulfur could be removed without devulcanization. Bedford and Gray[1] noted with unextracted rubber that the "ZnS" sulfur was from one-fourth to one-third the combined sulfur and they, as in the present research, used the ether-HCl method for determining this type of combined sulfur. The application of the short-path distillation and zinc removal techniques were tested in a stock consisting of unextracted crepe 100.0, TMTD 4.00 and ZnO 2.00. The results shown in Table II show that ZnS is not necessary as a product of vulcanization, since in this stock it was not even formed; yet the stocks had good properties even after complete removal of "ZnS" sulfur and nearly complete removal of zinc. Had ZnS been formed, it would have remained after the zinc removal treatment.

The data in Table II seem to refute the idea held by some that the state of vulcanization of rubber is due to the presence of zinc in the vulcanizate. The favorable effects of zinc oxide and zinc salts must then be due to their reactions during vulcanization.

The combined molar quantities of ZnDMDC, TMTM, and TMTU shown in Table I account for about 67 per cent of the TMTD compounded. No TMTD or free sulfur could be isolated from or detected in the distillate. The malodorous gaseous products, including H_2S and CS_2, were not isolated. The small amounts of TMTU and TMTM isolated from the distillate were estimated to represent one-half and two-thirds, respectively, of the amounts of these substances actually present. With these corrections the amounts of ZnDMDC, TMTM, and TMTU account for 77 per cent of the TMTD compounded.

The vulcanizate before and after distillation displayed a tensile strength of about 4000 p.s.i. and an elongation of about 750 per cent. After short-path distillation it aged rapidly, losing about half its strength during six months. This behavior is in sharp contrast to the usual good aging of TMTD unextracted rubber compounds.

When a TMTD 4 phr—ZNO 5 phr stock was given a "semicure" of 20 minutes at 280° F and then short-path distilled, the yield of TMTM was about three times the amount reported in Table I. This result, coupled with the inhibiting effect of TMTM on TMTD vulcanization, lends support to the idea that TMTD acts by disproportionation into TMTM and a polysulfide, as in reaction I.

$$2\,(CH_3)_2NC(S)SSC(S)N(CH_3)_2 \rightleftharpoons (CH_3)_2NC(S)SC(S)N(CH_3)_2 + (CH_3)_2NC(S)SSSC(S)N(CH_3)_2 \quad \text{(I)}$$

The tetramethylthiuram tri-, tetra-, and pentasulfides could not be isolated by Levi[1], though he succeeded in separating TMTD and the hexasulfide from the reaction product of ZnDMDC and S_2Cl_2. He found that the reaction product of DMADC with S_2Cl_2 contained TMTD and sulfur (S_8), but he was unable to isolate the hexasulfide from it. DMADC, being able to undergo interchange with various radiosulfur compounds (see Part II), thus may catalyze more effectively than ZnDMDC the disproportionation of the thiuram sulfides, and here may catalyze the disproportionation of tetrasulfide initially formed into TMTD and S_8. This catalytic action of the ZnDMDC appears to enable the reaction to go only as far as the hexasulfide.

The polysulfides thus are more unstable than TMTD and S_8. The trisulfide, for example, should be able to dehydrogenate the rubber to reform TMTD and liberate H_2S, as in reaction II, if chemical reactivity and instability go hand in hand. The rubber simultaneously may become cross-linked in this

$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 + \text{rubber} \longrightarrow (CH_3)_2NC(S)SSC(S)N(CH_3)_2 + H_2S + \text{dehydrogenated rubber} \quad \text{(II)}$$

operation, but this type of reaction is not known to be very effective for vulcanization. Another possibility that from our viewpoint is attractive is that the polysulfide is able to form TMTM and a copolymer of rubber with diatomic sulfur fragments, S_2, by reaction IIa. This copolymer under appropriate con-

$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 + \text{rubber} \longrightarrow (CH_3)_2NC(S)SC(S)N(CH_3)_2 + \text{copolymer of } S_2 \text{ and rubber} \quad \text{(IIa)}$$

ditions could liberate H_2S, a substance known to be reactive toward TMTD, and in this study found to be reactive toward TMTM.

REACTION OF HYDROGEN SULFIDE WITH TMTD AND WITH TMTM

From Bedford and Gray's work it is known that TMTD and H_2S form free sulfur and dimethyldithiocarbamic acid according to reaction III, the acid

$$(CH_3)_2NC(S)SSC(S)N(CH_3)_2 + H_2S \longrightarrow 2\ (CH_3)_2NC(S)SH + (S) \qquad \text{(III)}$$

being unstable. Because of their reactivity toward rubber, the sulfur atoms would not be expected to polymerize to S_8 in rubber. Rather they would be expected (1) to dehydrogenate the rubber (compare reaction II), (2) to copolymerize with rubber to form a vulcanizate (compare reaction IIa), or (3) to react reversibly with TMTM or TMTD to form higher sulfides. In the early stages of the process, when ample TMTM molecules are available, the reforming of TMTD molecules should be frequent. The possibility that the abundance of TMTM in the vulcanization process is lowered by the liberation of H_2S seemed to be worthy of study. A discussion of the reaction of H_2S with TMTM now follows.

The decomposition of TMTM at 140° C in the absence of rubber was found to be negligible, but when a slow stream of H_2S was passed for one hour through the molten compound (10.4 grams) at this temperature, reaction occurred with the evolution of CS_2 (89 per cent) and the sublimation of DMADC. The final product after distilling off the DMADC (1.29 grams, 15.5 per cent) was TMTU (85 per cent). Reactions IV and V evidently are the main overall reactions.

$$(CH_3)_2NC(S)SC(S)N(CH_3)_2 + H_2S \longrightarrow 2\ (CH_3)_2NC(S)SH$$
$$\downarrow$$
$$CS_2 + (CH_3)_2NC(S)SNH_2(CH_3)_2 \qquad \text{(IV)}$$

$$(CH_3)_2NC(S)SC(S)N(CH_3)_2 \longrightarrow CS_2 + (CH_3)_2NC(S)N(CH_3)_2 \qquad \text{(V)}$$

The mechanism by which H_2S might cause reaction V was found to be through the reactionof TMTM with DMADC produced by reaction IV. Thus, 9.35 grams (0.045 mole) of TMTM and 1.66 grams (0.01 mole) of DMADC were heated in a distilling flask to 140° C in an oil bath for one hour. During this time a slow stream of nitrogen was passed through the mixture and thence into a dry ice trap. The dry ice trap was found to contain 3.02 grams (88 per cent) of CS_2. The distilling flask was rinsed out with benzene to give a slurry which was then filtered. Solid DMADC amounting to 1.49 grams (90 per cent recovery) was thus obtained. The filtrate was distilled to supply 5.95 grams (100 per cent) of TMTU. Since Delépine[2] found that TMTM and dimethylamine react to form TMTU and DMADC, the action of the salt on TMTM may be ascribed to its decomposition into CS_2 and dimethylamine. This action is expressed by equations Va and Vb.

$$(CH_3)_2NC(S)SC(S)N(CH_3)_2 + 2\ HN(CH_3)_2 \longrightarrow$$
$$(CH_3)_2NC(S)N(CH_3)_2 + (CH_3)_2NC(S)SNH_2)CH_3)_2 \qquad \text{(Va)}$$

$$(CH_3)_2NC(S)SNH_2(CH_3)_2 \rightleftharpoons CS_2 + 2\ HN(CH_3)_2 \qquad \text{(Vb)}$$

As von Braun reported, DMADC may be distilled at reduced pressure. It may be assumed, however, that the vapor over the distilling salt contains only CS_2 and $(CH_3)_2NH$ molecules. Pure DMADC may be quickly heated to

about 140° C without melting, at which temperature violent decomposition into CS_2 and $(CH_3)_2NH$ ensues. Impurities in small amount lower the "melting point". The heating of dithiocarbamates of primary amines produces thioureas and hydrogen sulfide in good yield, but we have found in the case of the secondary amine salt DMADC that this type of reaction at 140° C is not appreciable even in the presence of sulfur or of H_2S.

In a further examination of the behavior of DMADC, it was heated at 140° C in a sealed tube with CS_2 for one hour. The experiment yielded free sulfur in 74 per cent yield and dimethylthioformamide in 89 per cent yield, based on reaction XII. This was an unexpected reaction and immediately

$$(CH_3)_2NC(S)SH \longrightarrow (S) + (CH_3)_2NC(S)H \qquad \text{(XII)}$$

DMADC (4 phr) was milled into extracted rubber and the mixture heated with CS_2 in the press at 318° F. There was no evidence of vulcanization and no odor of dimethylthioformamide. Therefore, it may be presumed that sulfur and the thioformamide were not liberated in the rubber.

Obviously, just because a reaction liberates sulfur in the absence of rubber, it does not follow that the reactants when heated with rubber will cause vulcanization or liberate sulfur. In this connection, though palmitic acid, zinc oxide, and zinc palmitate all liberate sulfur from TMTD, the reaction is too slow to account for vulcanization when these reagents and TMTD are heated with rubber. Actually, as stated in Part I, palmitic acid has little effect on TMTD vulcanization, whereas the zinc compounds are vigorous activators.

Dimethylthiocarbamyl dimethylsulfeneamide $(CH_3)_2NC(S)SN(CH_3)_2$ and dimethyl aminosulfide $(CH_3)_2NSN(CH_3)_2$, which are reaction products of TMTD (compare Part II) were found to be mild vulcanizing agents when heated with rubber in a concentration of 4 phr for 45 minutes at 287° F. The vulcanizates were transparent and similar in properties to rubber cured with peroxides. The sulfeneamide was also tested in the presence of 5 phr of ZnO, but then it failed to cause vulcanization. This result seems to eliminate the sulfeneamide as a possible intermediate in TMTD vulcanization but it is worthy of further study.

THE ACTIVATING EFFECT OF ZINC COMPOUNDS

An explanation of the beneficial effects of zinc compounds in TMTD vulcanization may now be examined. This explanation involves the action of hydrogen sulfide. Thus, it is to be noted at once that the reaction of dimethyldithiocarbamic acid produced by reactions III and IV with ZnO would form ZnDMDC, a stable end product. This reaction is important because TMTM is used up by reactions IV and V and, to the extent that these occur, TMTM is not available for reversing reaction I or for the prevention of higher thiuram polysulfide formation. H_2S is used up in IV but not in V. Bedford and Gray[3] found the complete removal of H_2S from the system to be unfavorable because TMTD vulcanization occurs by way of reaction III, but as shown by Booth and Beaver[4] the retarding or inhibiting action of H_2S in rather high concentration is quite general.

The pronounced tendency of H_2S to react superficially with ZnO was also mentioned by Bedford and Gray[3]. Their report that the reaction to form water is rapid, though incomplete, is confirmed by our experiments. When 16.30 grams (0.2 mole) of ZnO were treated with a slow stream of H_2S there was an almost immediate rise in temperature of about 10° C. Water was evolved, and

the increase in weight after 40 minutes amounted to 0.39 gram. During air drying for 48 hours, 0.06 gram of this increase was lost. As shown by the x-ray diffraction technique, the product contained a small amount of ZnS, and an electron diffraction study showed the surface to be ZnS. Calculated on the equation: $ZnO + H_2S \rightarrow ZnS + H_2O$, the net increase in weight amounts to the formation of 0.02 mole (10 per cent conversion) of ZnS. Very little reaction resulted during further treatment with H_2S.

That zinc compounds such as the oxide, palmitate, dithiocarbamate, and even the sulfide can contribute a buffering action on the concentration of hydrogen sulfide becomes evident by considering the distribution of zinc ions among the various anions that may be present in a TMTD-rubber mixture. The following reactions are formulated for such consideration. A further series

$$ZnO + H_2S \longrightarrow Zn\begin{matrix}OH\\SH\end{matrix} \longrightarrow ZnS + H_2O \qquad \text{(VI)}$$

$$Zn[OC(O)C_{15}H_{31}]_2 + H_2S \rightleftharpoons Zn[OC(O)C_{15}H_{31}]SH + HOC(O)C_{15}H_{31} \qquad \text{(VII)}$$

$$ZnS + H_2S \rightleftharpoons Zn(SH)_2 \qquad \text{(VIII)}$$

$$Zn(SH)_2 + Zn[SC(S)N(CH_3)_2]_2 \rightleftharpoons 2\,Zn(SH)SC(S)N(CH_3)_2 \qquad \text{(IX)}$$

$$Zn[SC(S)N(CH_3)_2]_2 + H_2S \rightleftharpoons Zn(SH)SC(S)N(CH_3)_2 + HSC(S)N(CH_3)_2 \qquad \text{(X)}$$

$$HSC(S)N(CH_3)_2 + ZnS \rightleftharpoons Zn(SH)SC(S)N(CH_3)_2 \qquad \text{(XI)}$$

of reactions of rubber as an acid (see Part IV) could be considered in relation to its effect on the H_2S concentration. Such an acid would enhance the behavior of the zinc compounds as buffers. Since the reactions leading to the formation of $Zn(SH)SC(S)N(CH_3)_2$ would not proceed to completion to anything like the extent of the reactions of ZnO and zinc palmitate with H_2S, the action of ZnS and ZnDMDC as activators would be expected to be relatively weak. This expectation was confirmed experimentally (see Part I), *i.e.*, ZnS and ZnDMDC were found to be weak activators in comparison to ZnO and zinc palmitate.

The buffering action of the zinc compounds on the H_2S concentration appears to allow the formation of cross-links containing one or two sulfur atoms as a result of reaction III, or as a result of reaction of the thiuram trisulfide with H_2S to liberate sulfur atoms two at a time. This follows because, in the absence of the buffering effect, the TMTM would be largely destroyed by reactions IV and V, and thiuram polysulfides containing many sulfur atoms, *e.g.*, the hexasulfide of Levi would result. These in comparison to the trisulfide should introduce more sulfur atoms per cross-link.

The availability of H_2S during TMTD vulcanization, being limited by the reactions just discussed, is believed to be so slight as to result in the addition of little of it to the polyisoprene double bonds. Hence, such addition could lead to the formation at most of only a few cross-links[5].

Because of the possible relation of zinc activation and TMTM consumption, the fate of TMTM in vulcanization was examined in a stock comprising extracted rubber 100, PBNA 1.00, TMTM 2.60, ZnO 5.00, and radiosulfur 0.40. Six sheets, 2.25 × 4.25 × 0.025 inches, were cured 10 minutes at 280° F. These sheets, which were fully cured, were then short-path distilled for five hours at 133° C, and at a pressure less than 0.001 mm. The products isolated

from the distillate were TMTM (43 per cent of that started with), ZnDMDC, and PBNA. The yield in moles of ZnDMDC amounted to 74 per cent of the number of moles of unrecovered TMTM. The radioactivities of the recovered TMTM, the ZnDMDC, and the starting sulfur are presented in Table III.

The radioactivity of the ZnDMDC in Table III is much too high and that of the recovered TMTM much too low for a random distribution of the isotopic sulfur atoms. In the TMTD synthesis, TMTM and S_8 are able to form a thiuram disulfide. The initial stage in this synthesis may be presumed to be a much higher polysulfide. It may also be presumed that this higher polysulfide could occur as an early state in TMTM-S_8 vulcanization. If the reaction of the thiuram polysulfide with the rubber is irreversible and fast when compared to the interchange of TMTM with thiuram polysulfide, then, in agreement with observation, the recovered TMTM should be less active than would be the case for a random distribution of the sulfur atoms. On the other hand, since it is known that TMTM and ZnO do not react with each other at curing temperatures, the formation of ZnDMDC with an activity higher than that corresponding to a random distribution of the sulfur atoms is significant. The

TABLE III

RADIOACTIVITIES OF SULFUR AND PRODUCTS OF THE TMTM RADIOSULFUR VULCANIZATION

Substance	Radioactivity (c/m) Found	Calcd.*
Radiosulfur	22,150	—
TMTM	1,260	2540
ZnDMDC	3,200	2320

* Assuming random distribution of the sulfur isotopes.

dithiocarbamic acid liberated by reaction IV would be radioactive in proportion to the activity of the H_2S produced from the vulcanizate. This activity alone would not be sufficient to account for the high activity observed for the ZnDMDC. However, a DMADC catalyzed interchange (see Part II) of the ZnDMDC initially formed with S_8* or with sulfur-rubber copolymer would do so. Some activity might also come from ZnDMDC formed by reaction of zinc oxide with hot thiuram polysulfides. On this basis it appears that thiuram polysulfide, H_2S, DMADC, and diemthyldithiocarbamic acid are essential intermediate products of the vulcanization reaction.

We have confirmed the report of Cummings and Simmons[6] that a TMTD stock may have similar stress-strain properties to one made by replacing the TMTD with a molecularly equivalent amount of TMTM and sulfur. Our TMTD stock containing 3.00 phr and TMTD and 5 phr of ZnO was fully cured after 40 minutes at 280° F, whereas the corresponding TMTM 2.60 phr sulfur 0.40 phr, and 5 phr of ZnO required only 10 minutes at the same temperature. We found the organically combined sulfur of the short-path distilled TMTM-sulfur stock to be 0.5 per cent or nearly twice that of the TMTD stock, which contained 0.28 per cent organically combined sulfur. The "ZnS" sulfur content was not more than about 0.1 per cent. This result is explainable on the basis that, although the number of cross-links (including C to C links) in one stock may be about equal to that in the other stock, the number of sulfur atoms per cross-link is greater in the case of the TMTM-S_8 stock. The poor quality of the zinc free TMTD-4.00 phr vulcanizate also may be ascribable to the presence

of a plurality of sulfur atoms per cross-link formed as a result of the reaction of higher polysulfides with the rubber.

APPLICATION TO THE THEORY OF VULCANIZATION

A complete theory of the structure of TMTD vulcanizates is beyond the scope of the present paper and this must, therefore, apply also to the mechanism of the vulcanization. However, a short discussion here may be warranted. The research up to this time indicates that TMTD alone is not able to fully vulcanize rubber unless a very large concentration is employed or even in the presence of ZnO if excess TMTM is present. Since TMTM should have no effect on the dissociation of TMTD into dithiocarbamate radicals, it is inferred, therefore, that these radicals, if formed, do not account for TMTD vulcanization. This effect of TMTM, however, in reducing the higher thiuram polysulfides to the disulfide stage, where vulcanization capacity is repressed to the degree that reactions other than vulcanization become predominant, suggests that sulfur atoms, one or two at a time, may copolymerize with polyisoprene[7]. Carbon to carbon bonds (suggested by Farmer[8]) could also be established. The source of the sulfur atoms may be by reaction III or the dissociation fragments of the thiuram trisulfide as indicated by reactions XIII and XIV (for pairs of sulfur atoms). Reaction XIV also accounts for the formation of TMTM.

$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 \rightleftharpoons \underset{\text{I}}{(CH_3)_2NC(S)SS\cdot} + \underset{\text{II}}{\cdot SC(S)N(CH_3)_2} \qquad \text{(XIII)}$$

$$(CH_3)_2NC(S)SSSC(S)N(CH_3)_2 \rightleftharpoons \cdot SS\cdot + (CH_3)_2NC(S)SC(S)N(CH_3)_2 \qquad \text{(XIV)}$$

The thiuram trisulfide, understandably, has not been isolated, presumably because of its instability[1]. This compound would not be capable of resonance stabilization to anything like the degree that obtains in the case of the thiuram disulfide (compare Part II). It is presumed that a main reaction of radical II is dimerization to form TMTD, which seems to be a relatively ineffective vulcanizing agent. Radical I could initiate polymerization by reacting with polyisoprene to form radical III. This radical could dimerize to form a cross-

III $\quad -CH_2-\overset{CH_2}{\underset{}{C}}(SSC(S)N(CH_3)_2)-CH-CH_2-$ $\qquad$ $-CH_2-\overset{CH_2}{\underset{}{C}}(SS\cdot)-CH-CH_2-$ $\quad$ IV

link or it could react with II to produce IV and TMTM. The polymerization of IV would form a chain of cross-links. Radicals III and IV also are presumed to be active enough to initiate polymerization of polyisoprene segments, thus forming C to C bonds. In this way a multiplicity of cross-link chains could be formed. It is to these polymer and copolymer chains, more or less normal to the rubber chains, that the characteristic properties of TMTD vulcanizates are believed due. These chains and the dimer of III would thus end in the grouping—$SSC(S)N(CH_3)_2$. This grouping suggests a reason for the usual good aging properties of TMTD vulcanizates and for the poor aging observed for the short-path distilled TMTD vulcanizates. Thus by a decomposition, appropriately slow, TMTD and sulfur fragments could be formed in the undistilled stock. These products by breaking peroxidation chains or by continued vulcanization would have the effect of preserving the rubber. During short-path distillation, the dimethyldithiocarbamyl sulfide end groups would be replaced by double bonds, with formation of ZnDMDC, ZnS, etc. In the

distilled vulcanizate, where the TMTD molecules and sulfur fragments would not be available, peroxidation and degradation of the rubber would occur uninhibited. Furthermore, the newly formed double bonds would be of a type different from the polyisoprene type and would, therefore, serve as active centers for degradative oxidation.

The buffering effects of zinc compounds thus seem to account for activation of TMTD vulcanization and to be closely related to the exceptional aging properties of TMTD vulcanizates. This circumstance supports the concept that vulcanization, including that with elementary sulfur, is a type of polymerization, since it is well known that sulfhydryl compounds may exert both initiating and inhibiting effects, *i.e.*, "modifying" action, on polymerization. Such effects appear clearly analogous to the activating and inhibiting effects on vulcanization of sulfhydryl compounds such as H_2S, dodecanethiol, and presumably, dimethyldithiocarbamic acid. Whether or not this analogy can be sustained by further work, it seems likely that vulcanization is a radical reaction which can be influenced by the buffering action of zinc compounds.

ACKNOWLEDGMENTS

The work described in this series of papers has been participated in by many individuals, including Earl Gregg, Donald Hay, Donald Beesing, Donald Kurtz, J. J. Shipman, Ray Fowler, W. S. Tyler, L. O. Schroyer, J. L. Barg, Dorothy Donnelly, Arthur Kuder. It was directed by W. L. Semon and J. M. Davies. The authors are grateful to H. E. Fritz for his support in this project.

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SPECIFIC HEAT OF NATURAL RUBBER *

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THE DERIVATION OF C_v FROM C_p

A detailed measurement of the specific heat (C_p) at constant pressure of natural rubber has been made by Bekkedahl[1]. For a theoretical treatment, however, the specific heat (C_v) at constant volume is more convenient. Therefore, we have calculated C_v from C_p by the thermodynamic relation:

$$C_p - C_v = v\alpha^2 T/\kappa \tag{1}$$

where v is the specific volume, α is the volume thermal expansion coefficient, and κ is the isothermal compressibility. The data of v and α are also given by Bekkedahl[2], but we cannot find the appropriate measurement of κ, so we have extrapolated the experimental formula for vulcanized rubber by Scott[3]. At the transition point at about 200° K, we used the Ehrenfest formula:

$$\Delta C_p = T(\Delta\alpha)^2/v\Delta\kappa \tag{2}$$

on the assumption that this transition is a transformation of the second order. Δ means the jump of those quantities at this point. Since ΔC_p and $\Delta\alpha$ are given in the data, $\Delta\kappa$ can be estimated by this formula.

At temperatures below 200° K, we neglect the variation of α and κ. From these considerations we get C_v at temperatures from 30° K to 320° K. (Figure 1).

Below 200° K this curve can be approximated by the combination of the Debye specific heat formula, choosing its characteristic temperature Θ_D = 110° K, and two Einstein formulas, choosing their characteristic temperatures $\Theta_{E^{(1)}}$ = 340° K, $\Theta_{E^{(2)}}$ = 1380° K and the number of oscillators 6, 21 (per isoprene), respectively. Of course these numerical values are nothing but a very rough approximation. However, in comparison with infrared absorption, it may be considered that they are the groups of normal vibration which have their frequencies near the above estimated values.

If we extrapolate this approximate formula above 200° K, and subtract it from C_v in Figure 1, we obtain the "additional specific heat" at the transition (Figure 3 solid line.) But since above 300° K some other vibrations may become excited, the additional heat curve must be steeper for the high temperature side, but the difference may be small near the transition point.

THEORY FOR THE ADDITIONAL SPECIFIC HEAT

With respect to the origin of the discontinuity of the specific heat of rubber at about 200° K, it has been thought that at this temperature the so-called micro-Brownian motion of the chain segment of the rubber molecule stops coöperatively, owing to some special properties of the intermolecular or intramolecular potentials acting between them, and it manifests itself as a trans-

* Reprinted from the *Journal of the Physical Society of Japan*, Vol. 3, Nos. 5–6, pages 305–307, September–December 1948.

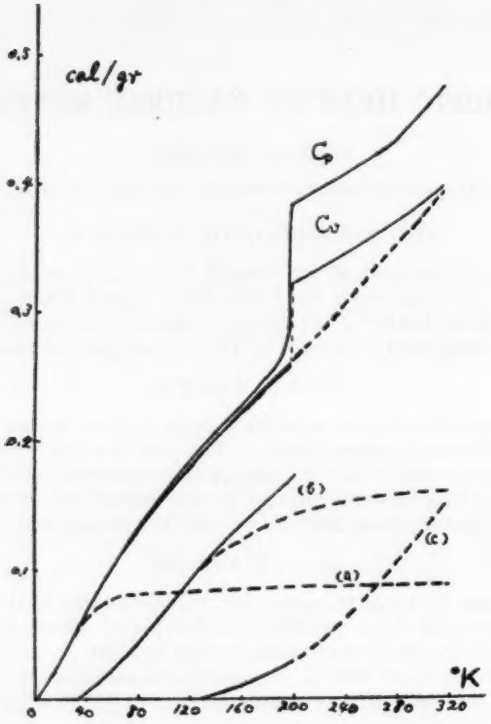

FIG. 1.

formation of the second order in the thermodynamical sense. Recently, however, Boyer and Spenser[4] have published a new idea. They consider this phenomena as an irreversible process, which depends essentially on the time rate of heating and cooling, and on the rapid increase in internal viscosity.

Here, we think that at least in the case of rubber, the former explanation is preferable, and in the following, we have calculated the additional specific heat due to the transition, according to this idea.

We assume that the unit volume of rubber contains N segments, vibrating as in the lattice model of liquids (for the present problem, the configuration of the chain is not important) and at about 200° K, these segments change from the state (I) of higher frequency to the state (II) of lower frequency on raising the temperature. We think of state (II) as the state of micro-Brownian motion, and the vibration of the internal degrees of freedom remain unchanged. We set N_1 and N_2 for the number of the segments which are in state (I) and (II) ($N_1 + N_2 = N$), and consider that they are packed together like the lattice whose coordination number is γ. So we can make an analogous treatment as in the theory of the binary alloy. The total energy of the intermolecular attraction W is given approximately by:

$$W = -2S_1\varphi_1 - 2S_2\varphi_2 - 2J\varphi_*$$

where $-2\varphi_1$ is the interaction energy of the segment pairs where both segments are in (I), s_1 is the number of those pairs, $-2\varphi_2$ and s_2 have similar meaning in (II), and $-2\varphi_*$ and J are the energy and the number of the pairs in which one segment is in (I) and the other in (II). We have the relations:

$$2s_1 = \gamma N_1 - J, \quad 2s_2 = \gamma N_2 - J$$
$$\gamma N = 2s_1 + 2s_2 + 2J$$

so we get:

$$W = -\gamma N\varphi_2 - \gamma N_1\varphi + Jw, \quad \varphi = \varphi_1 - \varphi_2$$
$$w = \varphi_1 + \varphi_2 - 2\varphi_* \tag{3}$$

The value of W is specified by N_1 and J. The number of configurations consistent with this energy may be taken as:

$$G(N_1, J) = h(N_1)\left(\frac{\gamma}{2}N\right)!2^J\left[J!\left(\frac{\gamma N_1 - J}{2}\right)!\left(\frac{\gamma N_2 - J}{2}\right)!\right]^{-1}$$

following Fowler and Guggenheim, the proportionality constant $h(N_1)$ being determined by the relation: $\sum_J G(N_1, J) = N!/N_1!N_2! \doteqdot G(N_1, J_0)$, where J_0 is the value of J by which G has the maximum value. It may be written as:

$$G(N_1, J) = \frac{N!}{N_1!N_2!}\cdot\frac{J_0!\left(\frac{\gamma N_1 - J_0}{2}\right)!\left(\frac{\gamma N_2 - J_0}{2}\right)!2^J}{J!\left(\frac{\gamma N_1 - J}{2}\right)!\left(\frac{\gamma N_2 - J}{2}\right)!2^{J_0}}$$
$$J_0 = \gamma N_1 N_2/N \tag{4}$$

Hence, the part of the partition function of the present system, relating to the transition is given by:

$$\Gamma(N_1, T) = \sum_J G(N_1, J)\exp\left[(\gamma N_1\varphi - Jw)/kT\right]\cdot(\Pi g_1)^{N_1}(\Pi g_2)^{N_2} \tag{5}$$

where g_1 and g_2 are the partition functions for vibrations which take part in this transition.

The free energy change ΔF by this transition is obtained from the relation $-kT\log T$. We can evaluate the summation by its maximum term as usual, so we have:

$$\Gamma(N_1, T) = G(N_1, J)\exp[(\gamma N_1\varphi - Jw)/kT)]\cdot(\Pi g_1)^{N_1}(\Pi g_2)^{N-N_1}$$
$$J = \frac{\gamma N_1(N - N_1)}{N}\frac{2}{\beta + 1}$$
$$\beta = \left\{1 + \frac{4N_1(N - N_1)}{N^2}(e^x - 1)\right\}^{\frac{1}{2}}$$
$$x = 2w/kT \tag{6}$$

and we can determine the equilibrium value of $s = N_1/N$ by the condition $(\partial\Delta F/\partial s)_T = 0$. The equation for determining s is:

$$\frac{\gamma}{2}\log\frac{\beta + (1 - 2s)}{\beta - (1 - 2s)} + \left(1 - \frac{\gamma}{2}\right)\log\frac{1 - s}{s}$$
$$= -\gamma\varphi/kT + 3\log\frac{(1 - \exp(-h\nu_1/kT))}{(1 - \exp(-h\nu_2/kT))} \tag{7}$$

here we set $(\Pi g) = (1 - \exp(-h\nu/kT))^{-1}$, assuming the Einstein model for molecular vibrations.

The additional specific heat ΔC_v may be obtained from:

$$\Delta C_v = -T\left(\frac{\partial^2 \Delta F(s(T), T)}{\partial T^2}\right)\frac{\rho N_L}{mN} \tag{8}$$

where ρ is the density, N_L is the Loschmidt number, and m is the molecular weight of the segment.

To solve s explicitly from (7) is not easy, so we calculated the temperature variation of s, assuming the various constants as $\gamma = 10\varphi = 2kT_0$, $w = 0.23\ kT_0$, $h\nu_1 = 2kT_0$, $h\nu_2 = 0.65\ kT_0$, $\rho = 1$, $T_0 = 200°$ K. (Figure 2) The expression for ΔC_v is also very complicated, but the important terms are approximately:

$$\begin{aligned}\Delta C_v \fallingdotseq \frac{\rho k N_L}{m}\Bigg\{\Bigg[&-\gamma\varphi/kT + 3\left(\frac{h\nu_1}{k}\right)(\exp(h\nu_1/kT) - 1)^{-1} \\ &- 3\left(\frac{h\nu_2}{k}\right)(\exp(h\nu_2/kT) - 1)^{-1}\Bigg]\left(\frac{\partial S}{\partial T}\right) \\ &+ 3s\left(\frac{h\nu_1}{kT}\right)^2 \exp(h\nu_1/kT)(\exp(h\nu_1/kT) - 1)^{-2} \\ &+ 3(1-s)\left(\frac{h\nu_2}{kT}\right)^2 \exp(h\nu_1/kT)(\exp(h\nu_2/kT) - 1)^{-2}\Bigg\}\end{aligned} \tag{9}$$

If we take $m = 500$, this gives the broken line in Figure 3. This value of m corresponds to seven isoprene radicals. The value of m of the above magnitude is necessary to give the same trend as in the experiment. Of course, other

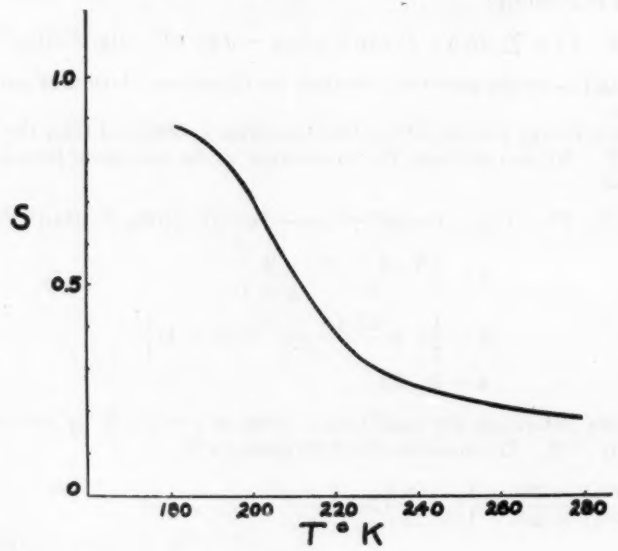

FIG. 2.

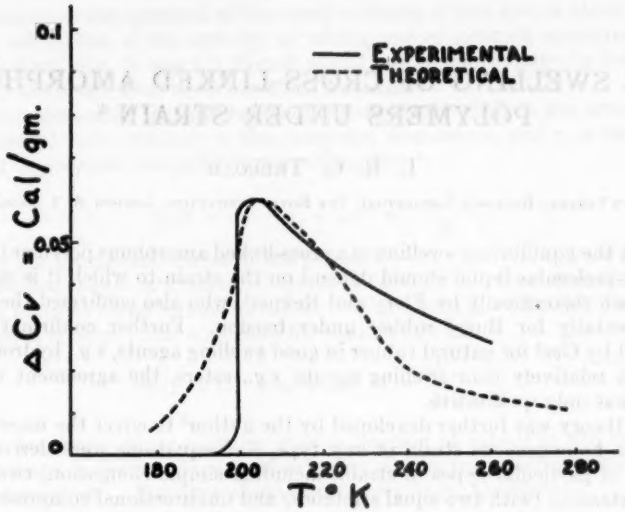

FIG. 3.

choices of the constants might be chosen, but in order of magnitude they would not be different from the results above.

Although our calculation is very rough, we think from these results that, in the transition, some of the vibrations in the group $\Theta_E^{(1)}$ change to micro-Brownian motion, raising the temperature.

CONCLUSIONS

From the above considerations, it may be said that the additional specific heat is the λ type and not a steplike type as might be assumed, and its origin is interpreted as a coöperative change of the vibrational state of the segments. We believe that similar phenomena of other high polymeric materials can be explained in the same manner.

SUMMARY

The constant volume specific heat of natural rubber is calculated from the constant pressure specific heat, which is measured experimentally, and it is shown that the low temperature part is expressed by a combination of the Debye and Einstein formulas. Some theoretical considerations on the transition phenomena at 200° K are included.

ACKNOWLEDGMENT

In conclusion, the author expresses his hearty thanks to Prof. T. Sakai for his kind guidance and to R. Kikuti and A. Ishihara for their valuable advice.

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THE SWELLING OF CROSS-LINKED AMORPHOUS POLYMERS UNDER STRAIN *

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That the equilibrium swelling of a cross-linked amorphous polymer in a suitable low-molecular liquid should depend on the strain to which it is subjected was shown theoretically by Flory and Rehner[1], who also confirmed their result experimentally for Butyl rubber under tension. Further confirmation was obtained by Gee[2] for natural rubber in good swelling agents, *e.g.*, hydrocarbons, but with relatively poor swelling agents, *e.g.*, esters, the agreement with the theory was only qualitative.

The theory was further developed by the author[3] to cover the more general case of a homogeneous strain of any type, and equations were derived for a number of particular types of strain, including simple elongation, two-dimensional extension (with two equal stretches) and unidirectional compression. It is the purpose of this paper to examine the swelling of vulcanized natural rubber under these three types of strain, and thus to provide a test of the more general theory. Two liquids, both good swelling agents, were used, *i.e.*, benzene and heptane.

The theoretical relations between swelling and strain.—The theoretical derivation of the equilibrium degree of swelling makes use of quantitative expressions, derived by statistical methods, for the free energy of dilution of the polymer chains by the low-molecular liquid (A_{om}) and for the free energy associated with the elastic network of long-chain molecules (A_e). The former is given by the well known Flory-Huggins equation[4] which may be written in the approximate form (valid for $v_r > 0.1$)

$$A_{om} = RT[\ln(1 - v_r) + v_r + \mu v_r^2] \qquad (1)$$

where v_r is the volume fraction of polymer in the swollen gel, R the gas constant per mole, T the absolute temperature, and μ a parameter which is specific to the particular polymer-solvent combination. The elastic network free energy is given by the statistical theory of rubber elasticity[5] as:

$$A_e = \frac{\rho RT}{M_c}(l_1^2 + l_2^2 + l_3^2 - 3) \qquad (2)$$

where l_1, l_2 and l_3 are the three principal extension ratios, referred to the unstrained unswollen dimensions, ρ is the density of the unswollen polymer, and M_c the molecular weight between successive points of cross-linkage (chain molecular weight). Using these expressions the relations given below are obtained for the swelling equilibrium under particular types of strain.

A modified formula for the entropy associated with the network expansion has recently been derived by Flory[6]. This yields a slightly higher dependence of equilibrium swelling on strain, the difference amounting to about 10 per cent in the slope of the curves over the range covered by the present experiments.

* Reprinted from the *Transactions of the Faraday Society*, Vol. 46, No. 9, pages 783–789, September 1950.

However, since the question of the relative merits of this and of other methods for the calculation of the entropy of mixing and of network expansion is still open to discussion, it was felt that it would not be appropriate, in the present context, to depart from the more usual formulas.

Simple elongation (or unidirectional compression).—If l_1, is the extension (or compression) ratio, referred to the unswollen dimensions, and v_r is the volume fraction of polymer at equilibrium swelling, then[3]:

$$\ln(1 - v_r) + v_r + \mu v_r^2 = -\frac{\rho V_0}{M_c}\cdot\frac{1}{l_1} \tag{3}$$

where V_0 is the molar volume of the solvent.

Two-dimensional extension.—This is defined as a state in which tensile stresses produce equal strains in the directions l_2 and l_3, while the stress in the direction l_1 is zero. The condition for equilibrium is[3]:

$$\ln(1 - v_r) + v_r + \mu v_r^2 = -\frac{\rho V_0}{M_c}\cdot\frac{1}{v_r l_2^4} \tag{4}$$

Free swelling.—Since v_r is the volume fraction of rubber in the mixture, it follows that $1/v_r$ is the volume in the swollen state corresponding to unit volume of the dry rubber. For unstrained swelling we have, therefore:

$$l_1 = l_2 = l_3 = 1/v_r^{\frac{1}{3}}$$

If in Equation (3) $l_1 > 1/v_r^{\frac{1}{3}}$ the stress is tensile, while if $l_1 < 1/v_r^{\frac{1}{3}}$ it is compressive. The condition for free swelling may, therefore, be obtained by putting $l_1 = 1/v_r^{\frac{1}{3}}$ in Equation (3), giving:

$$\ln(1 - v_r) + v_r + \mu v_r^2 = -\frac{\rho V_0}{M_c}\cdot v_r^{\frac{1}{3}} \tag{5}$$

A considerable amount of experimental evidence, which will not be reviewed here, has been adduced in support of the theoretical expressions (1) and (2) on which the theory of the swelling equilibrium is based. In connection with (1), reference may be made to the work of Gee and Treloar[7] and of Gee and Orr[8], which has been fully discussed[9], while the elastic network formula (2) has been substantiated experimentally by the author[10]. More direct evidence relating to the swelling behavior in the absence of strain, and the applicability of Equation (5), has been provided by Flory[11], Gee[2], and Flory, Rabjohn and Shaffer[12].

EXPERIMENTAL

The theoretical Equations (3), (4) and (5) contain two adjustable parameters, μ and M_c, the derivation of which must first be considered. In this connection it is to be noted that while the value of μ depends on the solvent used, that of M_c is determined only by the rubber, *i.e.*, for a given state of vulcanization. Moreover, if either μ or M_c is known, the other may be determined from a single measurement of the unstrained swelling equilibrium (Equation (5)). The following procedure was therefore adopted.

The value of μ for rubber and benzene has been determined directly from vapour-pressure measurements[9], and was taken as 0.41. From this, the M_c value for a particular sample of rubber swollen to equilibrium in benzene was calculated using Equation (5). Another sample cut from the same sheet, and having therefore the same M_c value, was swollen to equilibrium in heptane.

From Equation (5) the value of μ for heptane was thus found to be 0.42. This value was used in all subsequent experiments with heptane.

It should be noted that the values of μ and M_c were fixed either from vapor-pressure data or from the swelling equilibrium in the unstrained state. Their choice was thus entirely independent of the effect under investigation, *i.e.*, the effect of strain on the swelling equilibrium. Once these two parameters are chosen, however, the theoretical formulas (3), (4) and (5) define unique relations between the swelling and the applied strain.

It may also be pointed out that the effect of strain is not sensitive to small variations in μ and M_c. For example, in a two-dimensional extension in heptane, a 10 per cent reduction in μ (with a corresponding reduction in M_c to fit the unstrained swelling equilibrium) was calculated to increase the rate of change of swelling with strain l_2 by only 5 per cent.

Of the three types of strain chosen for the present experiments, the most serious difficulties were encountered with the two-dimensional extension. This type of strain will therefore be discussed first.

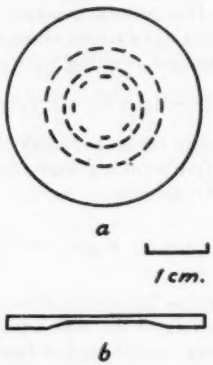

FIG. 1.—Rubber sample for 2-dimensional extension. (*a*) Plan; (*b*) Section.

Two-dimensional extension.—The stretching in two dimensions of a sheet of rubber, weakened by a high degree of swelling, in such a way that both the swollen volume and the degree of strain could be measured, presented a number of difficulties. After numerous ineffective trials, the following method was found to give a reasonably large strain before breaking occurred. The rubber sample was molded in the form of a disc, as shown in Figure 1, with a central portion 1 mm. thick and an outer region 2 mm. thick. The swollen rubber R (Figures 2*a* and 2*b*) was gripped by means of eight clamps C having a rounded profile as in Figure 2*b*, disposed around the circumference. The tightness of clamping was controlled by means of spacing washers of suitable thickness. (This was very critical: if clamped too tightly the rubber broke prematurely; if too loosely, it tended to slip out.) The mechanism for stretching the rubber consisted of an outer ring O which could be rotated with respect to the metal disc D by means of the ratchet mechanism M (details not shown).

The clamps were attached to points on the outer ring by means of standard steel wires passing over eight pulleys P mounted on the inner disc; rotation of the outer ring in the direction of the arrow thus imparted an equal radial motion to

each of the clamps. Means were provided for releasing the ratchet when it was desired to reduce the strain.

The swelling ratio was determined from measurements of the dimensions of the test-piece in the strained swollen state. For the measurement of the thickness, the metal disc A (Figure 2*b*) of 0.5 inch diam. was arranged so as to make a very light contact on the under surface of the strained sheet. A dial gauge, accurately mounted on the outer ring O by a reproducible 3-point support, was then brought down on to the upper surface, the difference of readings with and without the rubber in position giving the required thickness.

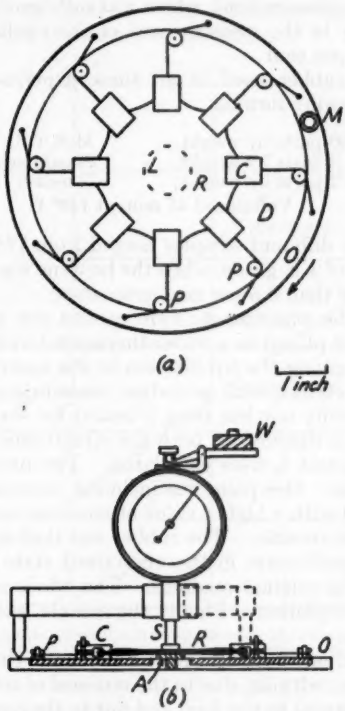

FIG. 2.—The stretching mechanism. (*a*) Plan; (*b*) Sectional elevation, showing gauge in position.

The dimensions in the plane of the sheet were obtained from measurements with a travelling microscope on reference lines L marked on the sheet as shown in Figure 2*a*. Some difficulty was experienced in obtaining a marking ink which would resist the solvent; the method adopted was to apply a solution of lead acetate in pyridine by means of a pen, and to develop this, before it had dried, in H_2S, thus producing insoluble lead sulphide[13].

Accuracy of measurement.—The least accurate dimensional measurement was the thickness measurement, and the reliability of this was the controlling factor in the accuracy with which the swelling ratio could be determined. Special attention was, therefore, given to possible errors in this measurement. The

dial gauge itself was graduated to 0.01 mm. and readings could be estimated to 0.001 mm. To reduce the effect of compression of the rubber by the foot of the gauge, the spring which provided most of this pressure was removed. The residual pressure, due to the weight of the center spindle S (Figure 2*b*) and the hairspring, was partly counterbalanced by a weight W of 17 grams applied to the lever arm operating the gauge. The final mean pressure thus obtained (as measured by means of a balance) was 8 grams; this could not be further reduced because of the uncertain friction in the mechanism. A pressure of 8 grams, corresponding to a stress of 12 g.-cm.$^{-2}$, was found experimentally, in a typical strained swollen sheet, to lead to an error of 0.005 mm. in 1.4 mm. or 0.36 per cent in the thickness measurement, which was sufficiently small to be neglected. The overall accuracy in the measurement of the swelling ratio was probably rather better than 1 per cent.

Materials.—The rubber used in all these experiments was compounded according to the following formula:

Smoked sheet	100 parts by weight;	M.B.T.S.	1 part by weight;
Sulfur	2 parts by weight;	Stearic acid	0.5 part by weight;
Zinc oxide	2 parts by weight;	Nonox-S	0.5 part by weight;

Vulcanized 45 min. at 140° C

The values of M_c for different samples ranged from 7740 to 8520.

The benzene was of A.R. grade, while the heptane was of a commercial grade, stated to contain less than 0.5 per cent aromatics.

Procedure.—All the experiments were carried out with the apparatus immersed in solvent and placed in a water thermostat at 20° C. After an initial swelling (1–3 days), giving the equilibrium in the unstrained state, the sample was clamped and stretched, with periodical measurement of dimensions, for a sufficient time (generally not less than 5 hours) for the attainment of equilibrium. From the final dimensions both the equilibrium swelling ratio and the stretch ratio in the sheet l_2 were calculated. The process was then repeated with increasing strains. One point was included, however, in which the equilibrium was approached with a higher value of strain to make sure that the points obtained were truly reversible. The rubber was then released, and the dimensions and swelling equilibrium in the unstrained state again measured; these were very close to the original readings. The whole set of readings required 2 or 3 days for its completion. Finally the sample was dried and again measured.

Two minor corrections were introduced. Firstly, there was a loss of volume of about 2 per cent on redrying, due to the removal of soluble ingredients. The swelling ratio was referred to the final and not to the original volume of the dry rubber. Secondly, there was evidence of slight anisotropy in the original sample, since on swelling the thickness dimension increased a little more (1 or 2 per cent) than the lateral dimensions. Assuming that the swollen state most nearly represented the isotropic condition, the dimensions were corrected to take account of these small changes.

Typical result for both benzene and heptane are shown in Figure 3. This gives the swelling ratio, *i.e.*, the ratio of the volume of the swollen gel to the volume of the dry rubber, or $1/v_r$, as a function of the extension ratio in the plane of the sheet, referred to the unstrained dry rubber.

Simple elongation.—The technique of measurement of simple elongation was similar to that employed in the two-dimensional extension, except that the stretching device was simplified. The sample was in the form of a parallel-

sided strip of approximate length 30 mm., width 7 mm. and thickness 1 mm., held in clamps having the form shown in Figure 2*b*. The length measurement was made on a central region (12 mm. in length before swelling) marked out by two reference lines equidistant from the clamps. Both width and thickness were measured in the strained swollen state. (The latter was not essential, but comparison of the dimensional changes in these two directions provided a useful check on the general accuracy.)

The procedure was in all respects similar to that described above, except that a shorter time (3 hours) was needed for the establishment of equilibrium. Corrections were applied as before for the slight anistropy of the sheet, and for the removal of solids by the solvent. The results are reproduced in Figure 4. Again, the agreement with the theory is very close.

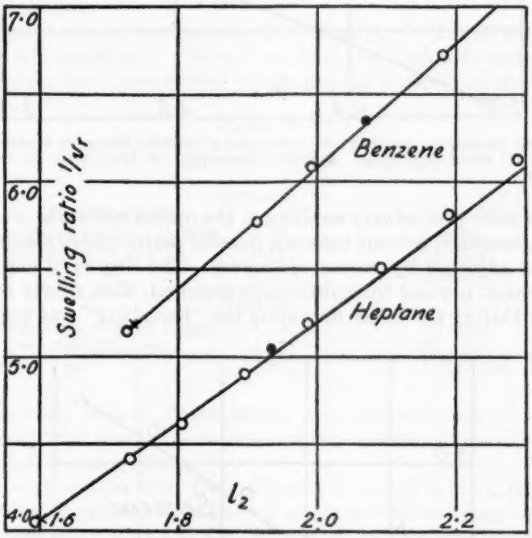

FIG. 3.—2-Dimensional extension. Swelling ratio as function of extended dimension l_2 referred to unstrained, unswollen state. ○ Strain increasing. ● Strain decreasing. × Final state on removal of stress. Curves theoretical.

Unidirectional compression.—This proved to be the least accurate of the three measurements for two reasons. First, the swelling ratios were determined by removal of the specimen from the solvent, superficially drying and weighing —a process not susceptible to the highest accuracy. Secondly, the samples used, being in the form of cylinders 1 cm. high and 1 cm. diam., required about 3 days to reach equilibrium, so that a total time of 2 weeks or more was required for a set of data. During this time there was a slow drift in the swelling ratio, which led to an appreciable uncertainty, particularly in benzene. This is discussed below.

Apart from these difficulties, the application of a perfectly homogeneous compressive strain itself presents a problem, since on account of end friction a cylinder compressed axially between parallel plates tends to deform to a nonuniform barrellike shape. This was largely avoided by the following device.

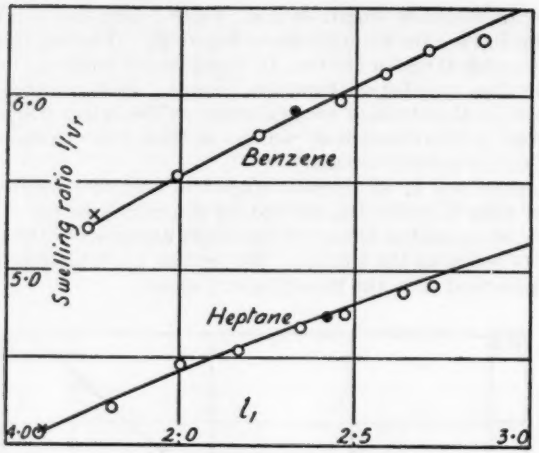

FIG. 4.—Simple elongation. Swelling ratio as function of extended dimension l_1 referred to unstrained, unswollen state. ○ Strain increasing. ● Strain decreasing. × Final state on removal of stress. Curves theoretical.

The cylinder, after preliminary swelling in the unstrained state, was compressed while still immersed in solvent between parallel plates whose distance of separation could be adjusted by means of screws. The degree of compression was carried somewhat beyond that ultimately required, then slowly reduced to the final value. During the latter operation the "barrelling" was greatly reduced,

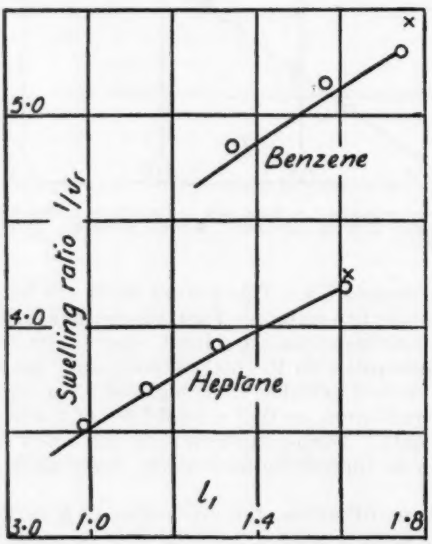

FIG. 5.—Compression. Swelling ratio as function of compressed dimension l_1 referred to unstrained, unswollen state. × Final state on removal of stress. Curves theoretical.

and this tendency was enhanced by the subsequent outward diffusion of solvent due to the application of the compressive stress. Indeed, it was quite possible in this way to produce an opposite state in which the middle diameter was smaller than the end diameter. With a little adjustment, the conditions required for the attainment of a substantially uniform cross-section could thus be achieved.

The points on each of the curves of Figure 5 were obtained with a single sample subjected to increasing compressions and finally returned to the unstrained state. After subsequent drying the weight and density of the sample were determined and these, in conjunction with the measured densities of the solvents, were used for the calculation of the swelling ratios. Figures are given in Table I for the change in the unstrained swelling ratio between the initial and final states, together with corresponding data for control samples not subjected to compression.

The difference between the increments of swelling for the strained and control samples is not significant. It is, therefore, reasonable to assume that the divergence between the experimental points and the theoretical curves of Figure

TABLE I

CHANGES IN SWELLING RATIO WITH TIME

Compressed sample		Control	
Benzene			
Before straining, swollen 5 days	5.30_4	5 days	5.31_8
Finally, total time 14 days	5.44_2	14 days	5.41_7
Difference	2.6%	Difference	1.9%
Heptane			
Before stretching, swollen 5 days	4.19_3	5 days	4.02_7
Finally, total time 31 days	4.24_3	26 days	4.06_4
Difference	1.2%	Difference	0.9%

5, which is relatively serious with benzene, may be attributed to this slow increase of swelling with time of immersion in the solvent, which occurs whether or not the rubber is under strain.

Conclusion.—It will be seen from Figures 3, 4 and 5 that, for the liquids chosen in this investigation, the effect of strain on the swelling equilibrium is satisfactorily accounted for by the statistical theory, under the three entirely different types of strain examined. In view of the simplifying assumptions introduced into the model on which the statistical calculations are based, however, an exact agreement between theory and experiment is hardly to be expected, and the close agreement actually found, *i.e.*, to within 5 per cent in the slopes of the swelling-strain curves, must be regarded as to some extent fortuitous. It is to be noted, for example, that in the study of the elastic properties of pure gum rubbers, significant departures from the theoretical form (2) for the network entropy have been observed[10]. With this reservation, however, the conclusion to be drawn from the present experiments is that the equations set out above provide a satisfactory quantitative interpretation of the dependence of the equilibrium swelling on a strain of the most general type.

SUMMARY

The equilibrium swelling of vulcanized natural rubber in benzene and heptane was investigated experimentally as a function of the state of strain. Three types of strain were examined, *i.e.*, simple elongation, 2-dimensional extension,

and unidirectional compression. The swelling ratios were determined either from measurements of linear dimensions, or by weighing, precautions being taken to ensure uniformity of the strain over the measured region. Measurements of swelling ratios were reproducible to about 1 per cent and the swelling process was completely reversible (with respect to strain variations). Changes in swelling ratios of up to 50 per cent were observed, the swelling increasing under tensile stresses and falling under compressive stresses. The results were accurately accounted for by the author's extension of the Flory-Rehner statistical theory, using two independent parameters—one the μ-value in the Flory-Huggins equation for the free energy of mixing, which was obtained from vapor pressure data; the other, the degree of cross-linking, which was determined from the swelling of the unstrained rubber. It is concluded that, for good swelling agents, this theory is applicable to a homogeneous strain of the most general type.

ACKNOWLEDGMENTS

The author desires to express his thanks to Dr. G. Gee for the provision of the rubber samples used in this work, and for a number of valuable discussions on the subject matter of this paper.

The author is also indebted to the British Rayon Research Association for enabling the work, which was done in the Davy Faraday Laboratory of the Royal Institution, to be carried out.

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POWER FACTOR AND VULCANIZATION *

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INTRODUCTION

Electromagnetic waves through a wide frequency range can be employed to give fundamental information on the structure of dielectrics. Electrons absorb in the visible; atoms in the infrared. Absorption by the electrical dipoles, postulated in Debye's theory[1], occurs at longer wave lengths, in the short radio waveband, and beyond. Thus, on going from higher to lower frequencies, the response is from larger units in the structure, electrons, atoms, intermolecular, and even more macroscopic effects.

In studying vulcanization by the measurement of electrical power factor, one is concerned with dipole effects. According to the Debye theory, the energy loss passes through a maximum at a frequency corresponding to the relaxation time of the material. In the case of most practical dielectrics, *e.g.*, natural rubber, the simple Debye theory has to be extended to a form which visualizes a range of relaxation times. An important empirical equation is due to Fuoss and Kirkwood[2], *viz.*,

ϵ' tan δ_f = A sech (α log$_e f$(max.)/f) where tan δ_f is the power factor at frequency f, ϵ' is the dielectric constant and α is a parameter which measures the breadth of the distribution of relaxation times. $\alpha = 1$ for a single relaxation time, and is smaller as the distribution is broader.

In addition to the absorption due to dipoles, there is a further broad absorption at lower frequencies still. This band is attributed to heterogeneity of the dielectric, *e.g.*, dispersed liquids or solids.

Unlike the absorption effects due to electrons and atoms, which occur at definite frequencies, the absorption by dipoles and larger structural units is dominated by frictional effects; any parameter which affects the internal viscosity alters the frequency of maximum loss.

Analogous mechanical hysteresis effects occur with natural and synthetic rubbers and rubberlike materials, and have been examined by Kornfeld and Posnjak[3] with a dynamic test operating at about 30 c/s. and are also referred to elsewhere[4]. In both the electrical and mechanical phenomena, the frequency of maximum absorption varies from megacycles at room temperature to much lower frequencies, 50–1000 c/s. at low temperatures. This field has been investigated by many workers, Roelig[5], Aleksandrov and Lazurkin[6], Zwikker[7], Zolotareva[8], Girard and Abadie[9], and others. A recent paper by Guth and coworkers[10] describes the effects of mechanical absorption at megacycle frequencies. The exact physical interpretation of this parallelism has not yet been found.

The present experimental work is concerned with the electrical effects accompanying vulcanization, a process previously investigated mainly from the

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 27, No. 1, pages 16–37, February 1951.

changes in mechanical properties. The absorption observed will be attributed to the sulfur dipoles formed during vulcanization, views put forward first by Kitchin[11] in 1932, and Curtis, McPherson and Scott[12] in 1933.

CHOICE OF COMPOUNDS

Cassie, Jones and Naunton[13] in the course of their work on fatigue in rubber employed power factor tests to study cure in tread stocks. The author in later work[14] on electrical properties showed that the changes taking place in carbon black stocks were much reduced at lower temperatures of cure, and in one case when the sulfur was omitted, the same changes in D.C. conductivity took place. It was, therefore, concluded that in the main these effects must be attributed to alterations in the carbon particle network arising from the heat applied during cure.

In relation to the present work, if electrical properties were to be used to follow the more fundamental chemical changes accompanying vulcanization, unfilled compounds were preferable. Stocks in general have been selected in line with modern rubber compounding as far as combined sulfur is concerned, *i.e.*, rarely exceeding 4–5 per cent. The work of Kitchin (rubber-sulfur stocks) indicated a rapid fall in the peak value of power factor (at 25° C) in the region below 12 per cent combined sulfur, but the frequency at which the peak occurred tended to be outside the range of his instrument (above 1 mc/s.). The development of the Marconi Q-meter made an investigation in this region possible.

EXPERIMENTAL METHOD

Apparatus Employed

The apparatus consists of a Marconi Q-meter[15] fed from an 80 VA constant voltage transformer T.F. 468A, and the detailed test procedure and method of calculation of power factor and dielectric constant is essentially that given in the Marconi instruction book. The method is based on the principle of the change of width of the resonance hump used and described by Hartshorn and Ward[16].

The frequency range employed is 0.1 Mc/s. to 40 Mc/s. Most of the important effects to be described occur at 10 Mc/s. or lower. It is probable that losses due to radiation and other stray effects become important at the highest frequencies and, in consequence, in this range the actual losses in the material under test may be overestimated.

Conditioning of Samples and Fixing of Electrodes

Test samples are molded discs 1.3 inch diameter and are of thickness approximately 2 to 3 mm. or portions of thin sheets of the same thickness. Samples are first of all cleaned carefully with ether applied with cotton wool, then tin foil discs of slightly greater diameter than the electrodes of the test jig (1.06 inches as compared to 1 inch) are affixed, using a smear of vaseline. All samples were conditioned for not less than 48 hours at 25° C and 75 per cent relative humidity. The test temperature was that of the laboratory, and was recorded with a thermometer placed at the side of the dielectric test jig.

Estimate of Errors

From a statistical examination of a large section of the present work, the standard deviation for a single observation was 0.05 per cent power factor. A

significant sampling error of the same order was also found. With the procedure adopted, three repeated tests were done on two samples from the same sheet and the six results averaged. For a 95 per cent significance level, a difference in two such means, *e.g.*, two cures must be 0.10 or greater.

In judging the degree of cure, the actual difference should be greater than this figure as the error of replicate cures has not been directly assessed in this work. An indirect estimate, however, can be formed by examination of the mean departure of experimental points from smooth curves such as in Figures 4, 6, 8, and 10, where 0.2 per cent power factor or less is usually significant. It is clear that the power factor test is capable of greater discrimination than routine chemical analysis and is much quicker to carry out. If, as in this work, such variables as temperature are not controlled, the strictest comparisons should be limited to work carried out on the same day, as 1° C can cause a 1 per cent change in the measured value of power factor.

EXPERIMENTAL RESULTS

PRELIMINARY WORK

Variation of Power Factor with Frequency

Figure 1 shows a collection of data illustrating the presence of a power factor maximum. It will be observed that with increase in combined sulfur the height of the maximum increases and the position shifts to lower frequencies. Note particularly M.6700 (90 rubber and 10 sulfur) as combination takes place. The shifts may be taken as evidence of (1) a decrease in the plasticizing effect of free sulfur (noted by Zolotareva[8]) as it combines with the rubber, and (2) an increase in the elastic effects due to sulfur combination. The results in general fit well on to the work of Kitchin.

Table 1 shows the other mixes selected to give a wide range of types of cure.

TABLE 1

M.5952	100 Rubber 5 Sulfur 1.25 Aldehyde-ammonia
M.5951	Same as M.5952, but with 5 zinc oxide added
M.9255	100 Rubber 3 Zinc oxide 1 Stearic acid 2.0 Sulfur 0.5 Mercaptobenzothiazole

Measurements at Constant Frequency 10 Mc/s

The following six stocks were examined over a range of times of vulcanization.

TABLE 2

	M.8140	M.8145	M.1337	M.1338	M.1339	M.1340
Rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	1	1	1	1
Phenyl β-naphthylamine	1	1	—	—	—	—
Sulfur	1	3	2.5	2.5	2.5	2.5
Mercaptobenzothiazole	0.5	2	—	0.75	—	—
Thiocarbanilide	—	—	1.5	—	—	—
Zinc diethyldithiocarbamate	—	—	—	—	0.375	—
Tetraethylthiuram disulfide	—	—	—	—	—	0.375

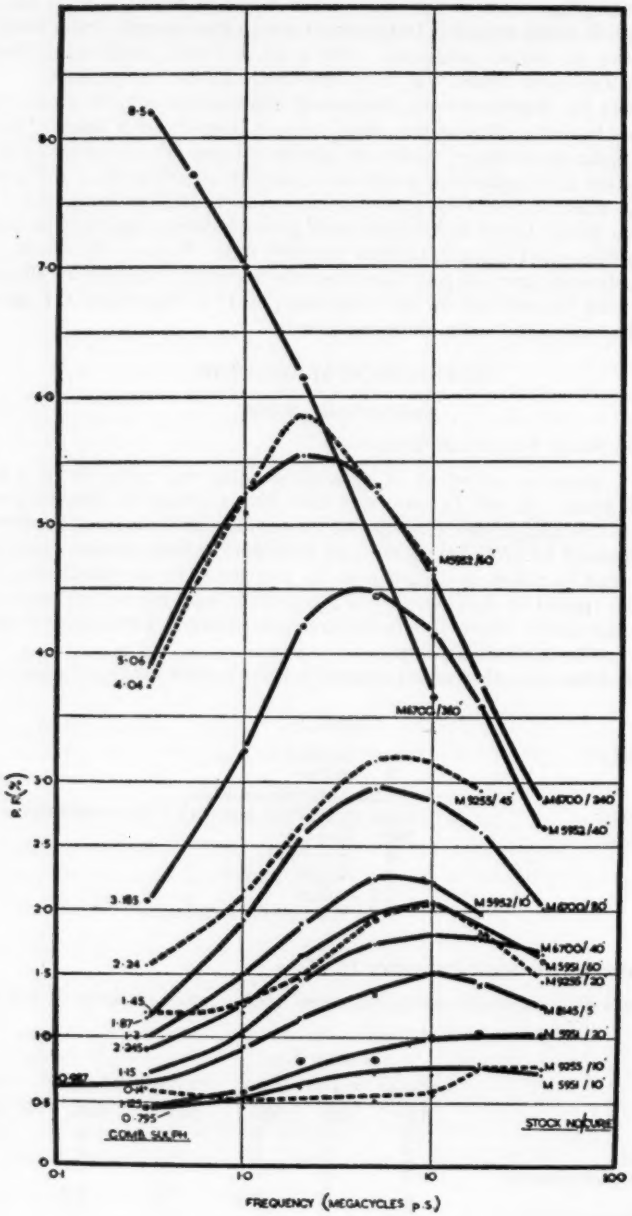
8·5
5·06
4·04
3·185
2·34
1·45
1·87
1·3
2·345
1·15
0·94
1·85
0·795
0·987
COMB. SULPH.
M5952/60'
M6700/360'
M9255/45'
M6200/240'
M5952/40'
M5952/10'
M6200/80'
M6700/40'
M5951/60'
M9256/20'
M8445/5'
M5951/20'
M9255/10'
M5951/10'
STOCK NO. 8
P.F.(%)
FREQUENCY (MEGACYCLES p.s.)
0·1
1·0
10
100

FIG. 1.

The results for P.F. (power factor) at 10 Mc/s. are given in Table 3 against time of cure compared with the change in other more usual properties, *e.g.*, tensile strength and combined sulfur (C.S.). The effects are shown more clearly for one mix (M.1338) in Figure 2.

TABLE 3

Mix	Temperature of cure (° C)	Time of cure (minutes)	P.F. per cent 10 Mc/s.	C.S. per cent	T_{30} (° C)	T.S. (kg. per sq. cm.)	Modulus 700 (per cent)	Linear swelling in C_6H_6	Resilience per cent (50° C)	Compression set
M.8140	141	5	0.5	0.26	—	—	—	—	—	—
		20	—	0.45	—	80	16	655	61.5	75
		30	1.14	0.66	—	100	32	565	66.0	52
		40	1.32	0.84	5.0	105	38	530	70.0	43
		60	—	0.95	4.5	125	46	500	73.5	38
		120	1.69	1.08	0.0	125	48	485	74.0	21
M.8145	141	5	1.51	0.83	5.0	115	48	—	75.5	100
		10	—	1.68	− 5.5	150	92	390	84.0	55
		20	3.28	2.42	−17.5	175	126	385	87.0	34
		30	3.68	2.88	−24.0	185	132	355	87.5	27
		40	—	2.92	−26.0	190	130	330	87.0	25
		60	—	3.01	−34.0	165	122	355	87.5	21
		120	4.11	3.10	−33.0	155	116	360	87.5	11
M.1337	130	15	1.14	0.66	8.5	90	31	670	48.5	63
		30	1.15	0.79	7.5	75	24	670	61.5	60
		60	1.30	0.72	—	80	22	675	60.0	57
		120	1.76	0.96	5	80	21	650	63.0	49
		240	2.01	1.32	2.5	80	25	595	65.0	36
M.1338	130	10	1.00	0.61	14.5	15	8	1000	48.5	96
		20	1.60	1.16	5.0	95	26	590	68.0	75
		40	2.12	1.79	− 2.5	145	54	455	77.0	43
		60	2.45	1.91	− 7.5	140	66	430	80.0	31
		120	3.18	2.46	−17.5	160	75	420	80.5	16
		240	3.32	2.57	−21.5	140	76	430	80.5	8
M.1339	130	5	1.48	1.09	6.0	125	62	480	76.0	75
		10	2.36	1.85	− 8.0	165	104	390	84.0	57
		15	2.87	2.30	−13.0	165	141	380	85.5	41
		30	3.22	2.45	−17.0	140	128	380	85.0	22
		60	3.35	2.46	−19.5	120	92	410	84.0	13
		120	3.80	2.55	−22	150	68	435	80.5	14
M.1340	130	5	0.53	0.19	—	—	—	—	—	—
		10	1.50	1.12	− 1	30	16	1100	60.0	—
		15	2.18	1.79	− 7.5	140	132	390	85.5	68
		30	3.10	2.44	−16.5	150	—	360	88.0	30
		60	3.35	2.55	−20	115	112	385	84.5	16
		120	4.10	2.61	−24	150	89	405	85.0	9

From these it can be seen that power factor changes closely follow other changes in physical properties, at least qualitatively; and the point where the rate of change of power factor with time of vulcanization markedly decreases coincides, in these cases, with choice of optimum cure from a study of other physical properties. Thus power factor measurements could be developed, if required, for very practical uses, *e.g.*, checking the vulcanization rate of suitable stocks before or during factory cure, etc. For example, in Table 4 data are

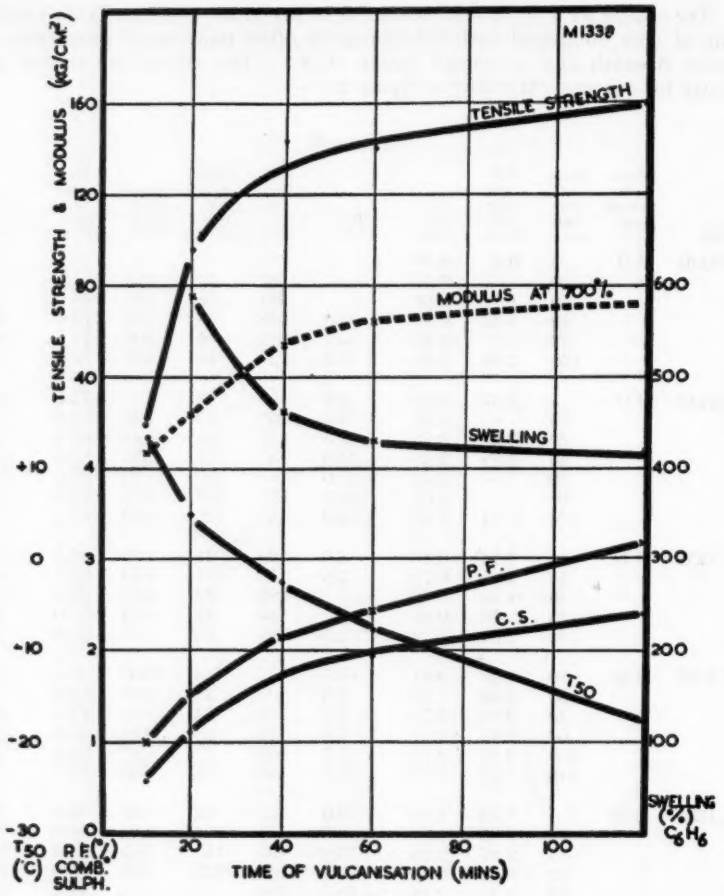

FIG. 2.

presented to illustrate how this could be done with sheets of a room temperature (25° C) curing stock. Data for relative swelling behavior in benzene are also given for comparison.

Effect of Other Ingredients

So far no account has been taken of any contribution to power factor which is likely to be made by other ingredients. In Table 5 data are presented to illustrate the contribution of various compounding ingredients to the power factor of an unvulcanized stock, and only in the cases where relatively large amounts of accelerator (zinc isopropylxanthate and diethylammonium diethyldithiocarbamate) were added has there been a significant contribution. This conclusion only applies to stocks free from fillers with large dielectric loss, *e.g.*, carbon black.

TABLE 4

Rubber	100
Zinc oxide	10
Blanc fixe	75
Stearic acid	1
Sulfur	2
Zinc isopropylxanthate	0.75
Diethylammonium diethyldithiocarbamate	0.25

Days of cure at 25° C	Power factor (per cent) 10 Mc/s. and laboratory temperature	Linear swelling (length of test strip after 5½ hrs. in benzene)
0	0.90	Soluble
1	1.35	Just cured
2	1.49	174
3	1.62	161
6	1.71	153
8	1.78	150
13	1.90	149
17	1.88	150

The data shown in Figure 1 in which decreasing combined sulfur below 10 per cent is accompanied by a fall in the peak value of power factors, suggested some relationship between these two properties. In Figure 3, combined sulfur has been plotted against maximum power factor (above power factor 3 to 3.5

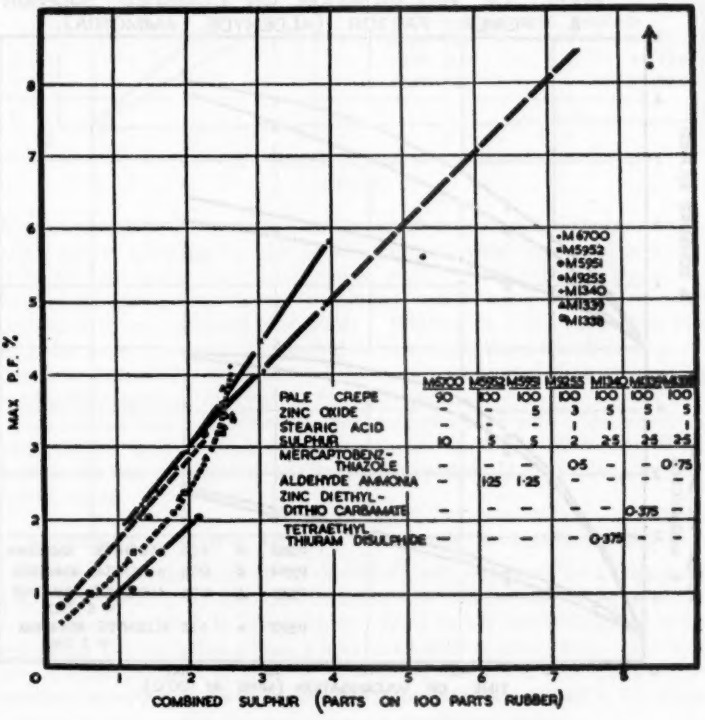

FIG. 3.

TABLE 5

ELECTRICAL PROPERTIES DUE TO COMPOUNDING INGREDIENTS (UNCURED STOCK)

Rubber	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	—	—	3	—	—	—	10	3	3	10	10
Blanc fixe	—	—	—	—	—	—	75	—	96	75	75
Stearic acid	—	1	—	—	—	—	1	1	1	1	1
Sulfur	—	—	—	0.25	2	8	4	2	2	—	2
Mercaptobenzothiazole	—	—	—	—	—	—	—	0.5	0.5	—	—
Zinc isopropylxanthate	—	—	—	—	—	—	—	—	—	2.5	1.25
Diethylammonium diethyldithiocarbamate	—	—	—	—	—	—	—	—	—	1.5	0.75
Power factor per cent at 10 Mc/s. and laboratory temperature	0.44	0.4	0.4	0.4	0.45	0.48	0.53	0.47	0.62	1.38	0.97

per cent) and against power factor at 10 Mc/s. for stocks of power factor 0 to 3.5 per cent where measurements were made at this frequency only. The point in the top righthand corner (M.6700—360′ cure) needs correction upwards (compare Figure 1).

Considering the graphs in Figure 3, it was thought at the time that, apart from M.5951 the curve for aldehyde-ammonia accelerator in the presence of

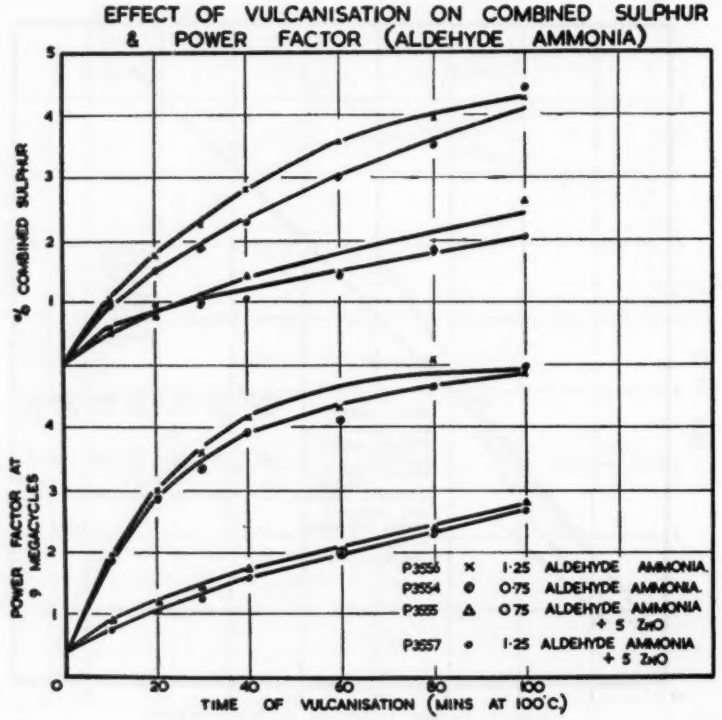
EFFECT OF VULCANISATION ON COMBINED SULPHUR & POWER FACTOR (ALDEHYDE AMMONIA)
% COMBINED SULPHUR
POWER FACTOR AT 9 MEGACYCLES
TIME OF VULCANISATION (MINS AT 100°C)
P3556 × 1·25 ALDEHYDE AMMONIA
P3554 ● 0·75 ALDEHYDE AMMONIA
P3555 △ 0·75 ALDEHYDE AMMONIA + 5 ZnO
P3557 • 1·25 ALDEHYDE AMMONIA + 5 ZnO

FIG. 4.

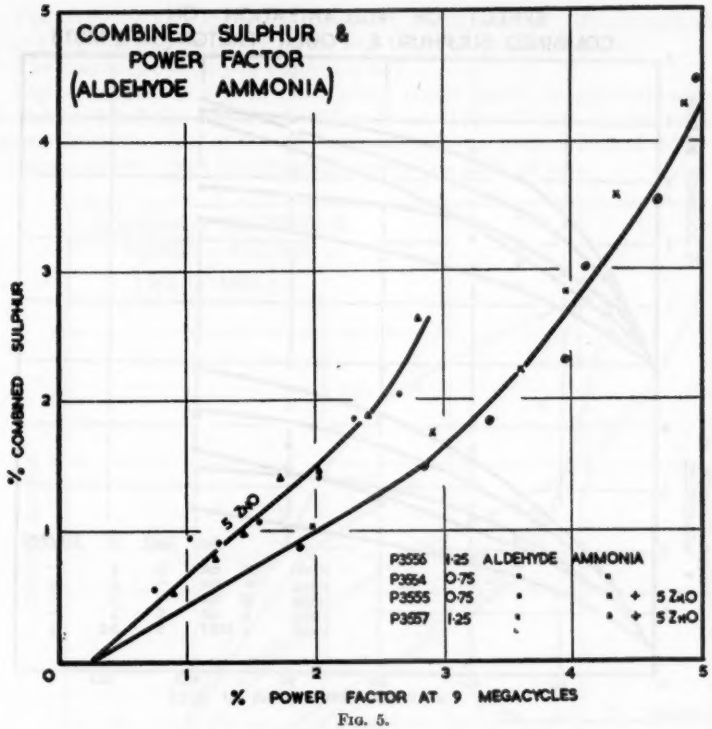

FIG. 5.

zinc oxide, the data for the other stocks might be accounted for by a single correlation curve, allowing for the possible experimental error (in general probably somewhat larger than in the main work). One anomaly stood out, the difference in the power factor combined sulfur relationship for aldehyde-ammonia with and without zinc oixde. Bearing in mind that these two sets of samples were processed and tested at the same time, the difference did not appear attributable to experimental errors and suggested that some at least of the sulfur is combined in a rather different way.

The stress-strain properties of stocks accelerated with aldehyde-ammonia in the presence and absence of zinc oxide are markedly different. The main investigation was undertaken to study this question further over a wider range of accelerators.

EXPERIMENTS WITH A NUMBER OF TYPICAL ACCELERATOR SYSTEMS

The experimental work to be described was restricted to a frequency of 9 Mc/s. By working at constant frequency a compromise is effected. Much less experimental work is involved, but for a strict proportionality with combined sulfur the variation of tan δ max/α should be considered. For the most accurate interpretation of the curves relating tan δ and combined sulfur, two corrections would have to be applied: (1) for converting tan δ to tan δ max, (2) for the alteration in the value of α as the percentage combined sulfur changes. From the data in Figure 1 α is found to vary from about 0.7 for 1 per cent C.S.

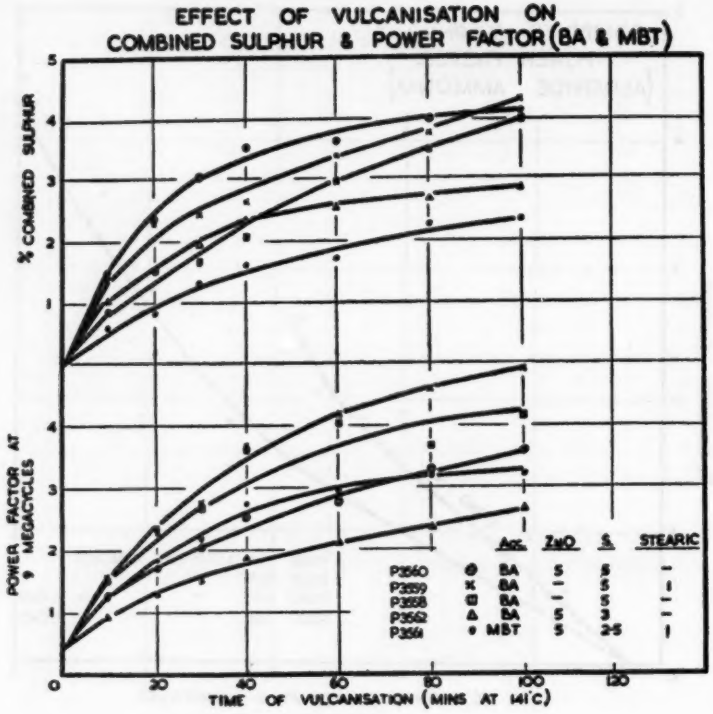
EFFECT OF VULCANISATION ON
COMBINED SULPHUR & POWER FACTOR (BA & MBT)
% COMBINED SULPHUR
POWER FACTOR AT 9 MEGACYCLES
TIME OF VULCANISATION (MINS AT 141°C)
Acc. ZnO S STEARIC
P3560 ● BA 5 5 —
P3559 × BA — 5 1
P3558 □ BA — 5 —
P3562 △ BA 5 3 —
P3561 ▲ MBT 5 2·5 1

FIG. 6.

to 0.5 for 4 per cent C.S. If a constant value of α is assumed, *e.g.*, say, 0.6, which is the value for about 2 per cent combined sulfur and f(max) near 9 M.C., then the two correction factors mentioned above tend to add for frequencies $f > f$ max and to cancel out for frequencies lower than f max. Therefore in plotting tan δ values at a constant frequency of 9 Mc/s. against combined sulfur, the line obtained tends to be straightened and only becomes markedly curved above about 3 per cent combined sulfur.

To assist with making the large number of test-samples required, thin sheets were cured in a window mold (approximately 2 mm. thick).

Basic Accelerator Types

Below is given a table of the mixes used:

TABLE 6

	P.3554	P.3555	P.3556	P.3557	P.3558	P.3559	P.3560	P.3561	P.3562
Rubber	100	100	100	100	100	100	100	100	100
Sulfur	5	5	5	5	5	5	5	2.5	3
Aldehyde-ammonia	0.75	0.75	1.25	1.25	—	—	—	—	—
Butyraldehyde-aniline	—	—	—	—	0.75	0.75	0.75	—	0.75
Mercaptobenzothiazole	—	—	—	—	—	—	—	0.5	—
Zinc oxide	—	5	—	5	—	—	4	5	5
Stearic acid	—	—	—	—	—	1	—	1	—

Test samples were cured for 10, 20, 30, 40, 60, 80, and 100 minutes at 141° C, and were tested for power factor and then for combined sulfur.

The results are shown in Figures 4 to 7.

Figure 4 shows the way in which power factor results for aldehyde-ammonia parallel in detail the combined sulfur data. The addition of zinc oxide decreases the initial rate of rise of both power factor and combined sulfur and, within the curing times investigated, lowers the state of cure.

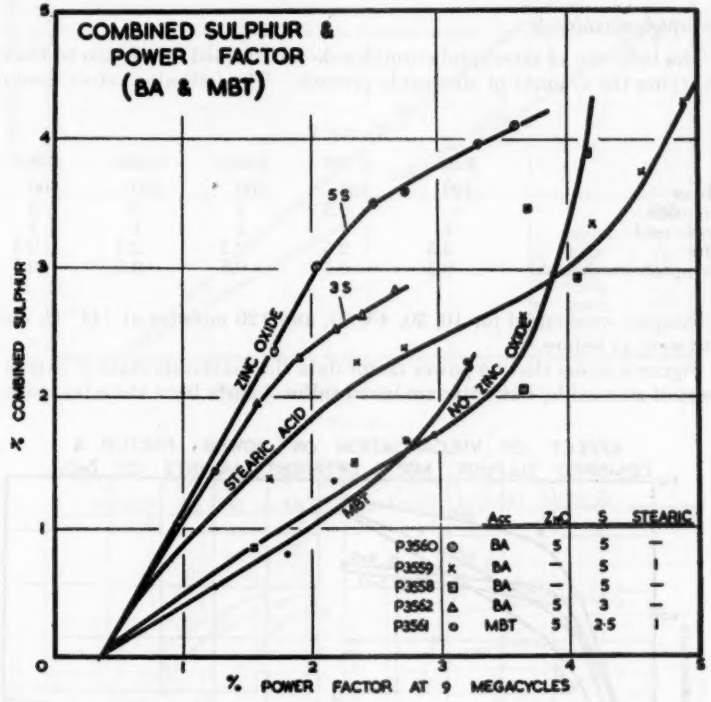
COMBINED SULPHUR & POWER FACTOR (BA & MBT)
5S
3S
ZINC OXIDE
STEARIC ACID
MBT
NO ZINC OXIDE
% COMBINED SULPHUR
% POWER FACTOR AT 9 MEGACYCLES
Acc ZnO S STEARIC
P3560 ○ BA 5 5 —
P3559 × BA — 5 1
P3558 ⊡ BA — 5 —
P3562 △ BA 5 3 —
P3561 ○ MBT 5 2·5 1

FIG. 7.

Figure 5 shows the correlation between power factor and combined sulfur. Up to at least 3 per cent power factor, the two sets of points with and without zinc oxide lie on two different straight lines.

Above 3 per cent, at any rate in the case of no zinc oxide, the curve tends to turn upwards, apparently indicating a smaller power factor increment for each new sulfur atom combined. In fact, most or all of the curvature can be accounted for by making estimated corrections for tan δ max. and α.

Figures 6 and 7 show the data for butyraldehyde-aniline. One curve for mercaptobenzothiazole is included to show where the normal acidic type lies in relation to the basic accelerators.

In the curves relating combined sulfur and power factor when zinc oxide is omitted, the same general behavior is shown as for aldehyde-ammonia. The curves with zinc oxide show an opposite trend curving towards the power factor axis. Reducing the amount of sulfur produces this turning over at an

earlier point, indicating some connection with shortage of sulfur. No detailed explanation can be given, but the suggestion is that under these conditions the type of combination is different and is of a kind which increases the power factor contribution per sulfur link. In this case, corrections applied for tan δ max. and α would tend further to increase the bending over towards the power factor axis. Stearic acid produces a curve intermediate in posi on and shape between those for mixes with and without zinc oxide.

Mercaptobenzothiazole

The behavior of mercaptobenzothiazole was studied in relation to the effect of varying the amount of zinc oxide present. The following mixes were used:

TABLE 7

	R.2836	R.2837	R.2838	R.2839	R.2840
Rubber	100	100	100	100	100
Zinc oxide	—	0.5	1	2	5
Stearic acid	1	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5	2.5
Mercaptobenzothiazole	0.5	0.5	0.5	0.5	0.5

Samples were cured for 10, 30, 45, 60, and 120 minutes at 141° C, and the tests were as before.

Figure 8 shows that on power factor data the maximum state of cure is with 1 part of zinc oxide, but with combined sulfur 2 parts have the advantage. In

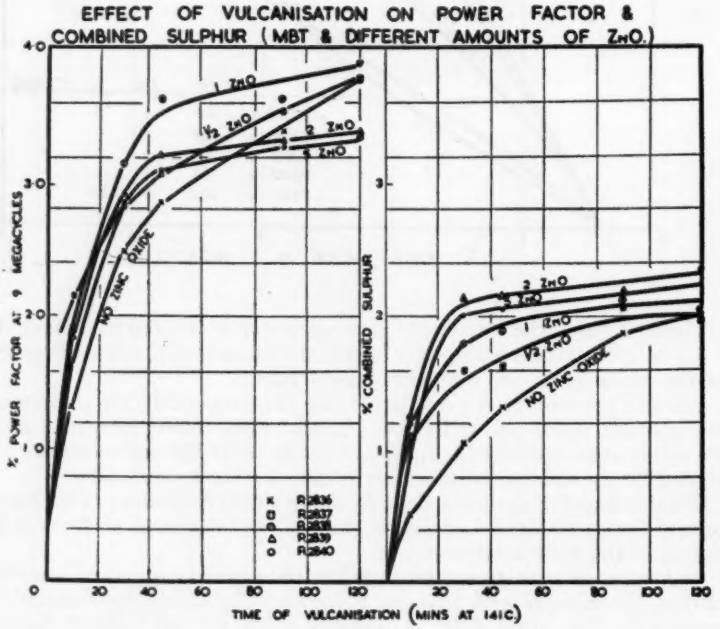

FIG. 8.

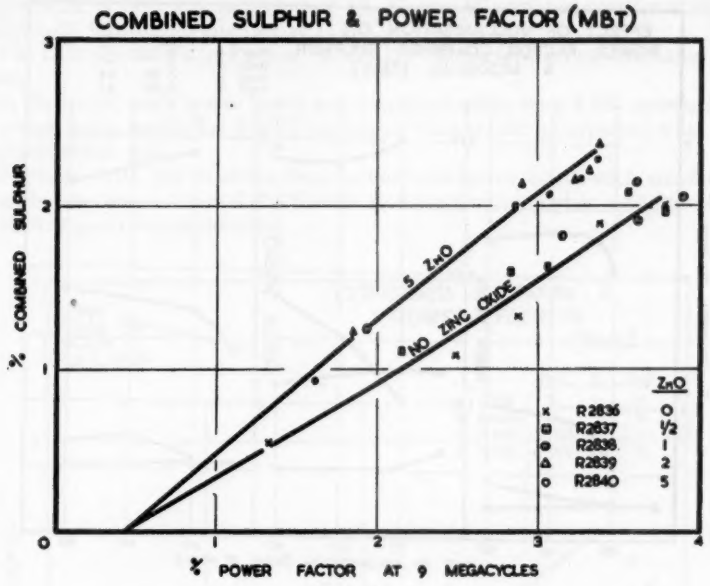
COMBINED SULPHUR & POWER FACTOR (MBT)
% COMBINED SULPHUR
% POWER FACTOR AT 9 MEGACYCLES
5 ZnO
NO ZINC OXIDE
ZnO
R2836 0
R2837 ½
R2838 1
R2839 2
R2840 5

FIG. 9.

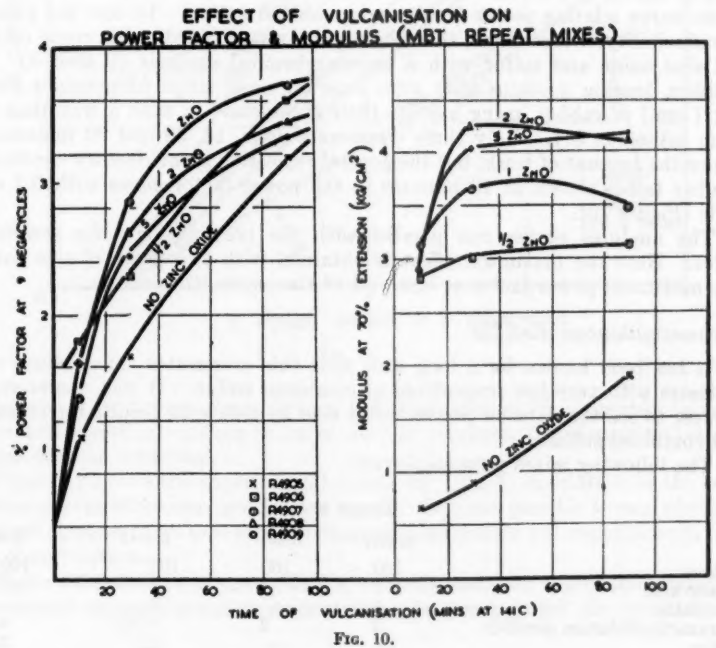
EFFECT OF VULCANISATION ON
POWER FACTOR & MODULUS (MBT REPEAT MIXES)
% POWER FACTOR AT 9 MEGACYCLES
MODULUS AT 70% EXTENSION (kg/cm²)
TIME OF VULCANISATION (MINS AT 141°C)
1 ZnO
2 ZnO
5 ZnO
½ ZnO
NO ZINC OXIDE
R4905
R4906
R4907
R4908
R4909

FIG. 10.

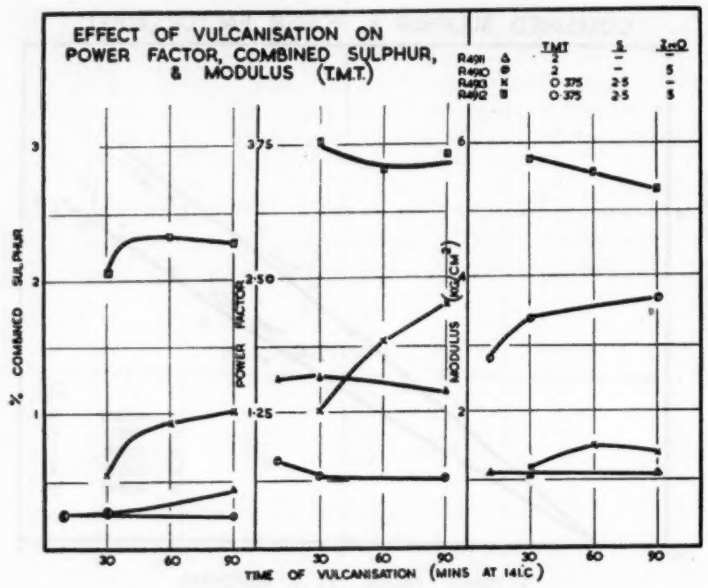

FIG. 11.

Figure 9 the data show that addition of zinc oxide causes anticlockwise rotation of the curve relating power factor and combined sulfur. To test the general reproducibility of the effects, this whole series was remixed, using crepe rubber and zinc oxide and sulfur with a known chemical analysis (R.4905–8). In addition, tension modulus tests were done on small strips (dimensions about 5 × 1 cm.) of rubber, using a Scott-Blair rheometal[17] in such a way that the beam ratio was 3:1. Only three cures were done, 10, 30 and 90 minutes to reduce the amount of work, but the general repetition is satisfactory—even the peculiar tail is shown at 10 minutes in the power factor curve with 0.5 zinc oxide (Figure 10).

The modulus curves run parallel with the previous data for combined sulfur. Here the maximum effect is obtained with two parts of zinc oxide. The maximum power factor at one part of zinc oxide still persists.

Tetramethylthiuram disulfide

It has been known for a long time that this accelerator can produce vulcanizates with very low proportions of combined sulfur. It was, therefore, of interest to see the data on power factor side by side with results for modulus and combined sulfur.

The following mixes were employed:

TABLE 8

	R.4910	R.4911	R.4912	R.4913
Rubber	100	100	100	100
Stearic acid	1	1	1	1
Zinc oxide	5	—	5	—
Tetramethylthiuram disulfide	2	2	0.375	0.375
Sulfur	—	—	2.5	2.5

Cures for R.4910 and R.4911 were 10, 30, and 90 minutes, and for R.4912, R.4913—30, 60, and 90 minutes at 141° C.

The data are shown in Figures 11, 12, 13. Some interesting anomalies are evident.

In Figure 11, while power factor and combined sulfur show a fair correlation, the power factor results for R.4911 are higher than would be expected from the combined sulfur data.

Similarly, with the modulus data, a fair correlation exists with combined sulfur, but in this case mix R.4910 tends to have a much higher modulus than the sulfur figures would indicate.

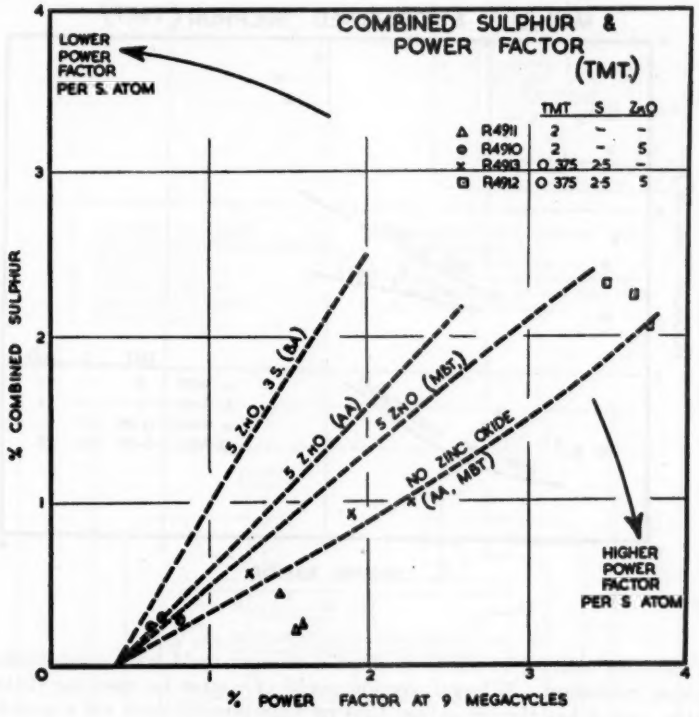

Fig. 12.

In mix R.4912 there seems to be a definite tendency for properties (power factor and modulus) to drop in cures over 30 mintues; this suggests that reversion may be occurring.

Figure 12 shows the experimental points for T.M.T. in relation to the correlation curves with other accelerator types. It is not possible to say whether chemical changes (such as reversion) or experimental error are responsible for the lack of correlation.

Figure 13 shows the poor correlation between combined sulfur and modulus. The dotted curves for mercaptobenzothiazole are included for comparison.

The points for no zinc oxide lie in the vicinity of the mercaptobenzothiazole curve. But the addition of zinc oxide raises the modulus well above the mercaptobenzothiazole curve.

THE EFFECT OF TEMPERATURE

The effect of temperature on power factor has already been mentioned. At the time the extent of the effect was not fully appreciated. Attempts were made, however, to follow the vulcanization of a mercaptobenzothiazole compound while cure was actually proceeding. Figure 14 shows the special cell

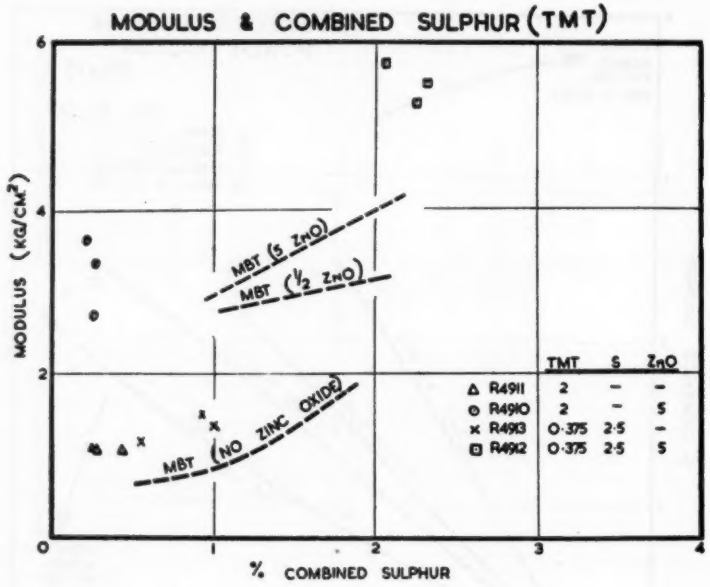

FIG. 13.

and screened lead. The cell is in effect a plunger mold with polytetrafluoroethylene insulation. A larger version could of course be used for dielectric heating, and it has the advantage that no high tension leads are exposed and the outside of both halves of the mold are earthed.

At 141° C, however, the standard gum mix was found to have no appreciable power factor. This indicated a much steeper change of power factor with temperature than had been anticipated from the frequency variation. Further exploration of the peak was, therefore, carried out using three frequencies, 9 megacycles and ½ megacycle on the Q-meter and 800 cycles on a Cambridge Schering bridge. The low temperature test cell is shown in Figure 15, and the results obtained over a temperature range are given in Figure 16 for both instruments.

An examination of this last graph (the ordinate ΔR indicates the change in the micrometer condenser readings, measured in 0.0001 inch) shows that the

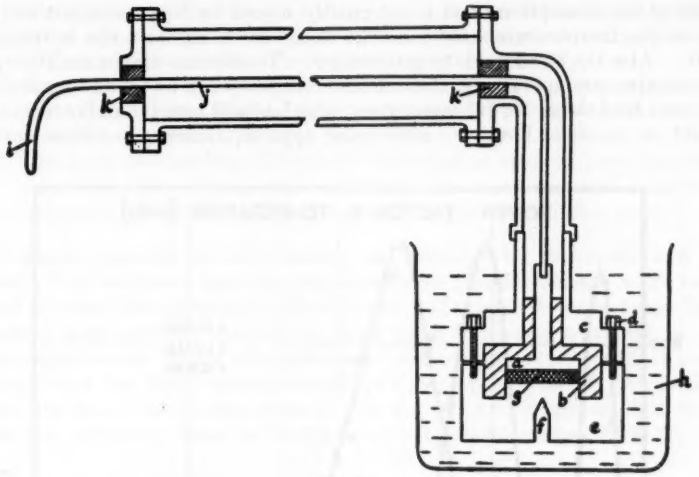

FIG. 14.

a Top electrode (brass).
b Polytetrafluoroethylene insulator.
c Pressure plate.
d Fixing screws.
e Bottom electrode.
f Thermocouple cavity.
g Rubber sample.
h Heating fluid (low molecular-weight polyisobutylene).
i Fixing to dielectric loss jig.
j Special (low capacity) connecting copper lead in earthed brass tube.
k Polyethylene insulators.

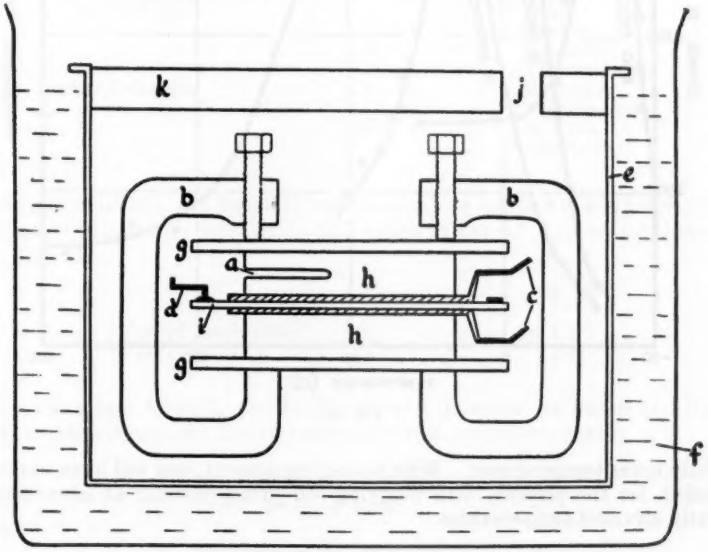

FIG. 15.

a Thermocouple cavity.
b "Perspex" clamps.
c Leads to tinfoil electrodes with aluminum backing plates.
d Tinfoil guard "ring" and lead.
e Hollow cylindrical brass container. "Drikold" cooling mixture.
g "Bakelite" plates.
h Circular polyethylene insulators.
i Circular rubber sample.
j Inlet for leads to thermocouple and electrodes.
k Rubber top.

height of the absorption band is not greatly altered by frequency, but the position on the temperature scale is moved about 60° C up for a rise in frequency of 10^4. Also the band tends to get broader. To obtain a maximum absorption at vulcanizing temperatures, the required frequency can be found by extrapolation, and is of the order 10^5 megacycles, which is well into the radar region. It should be possible, however, with radar type equipment, to follow cures at

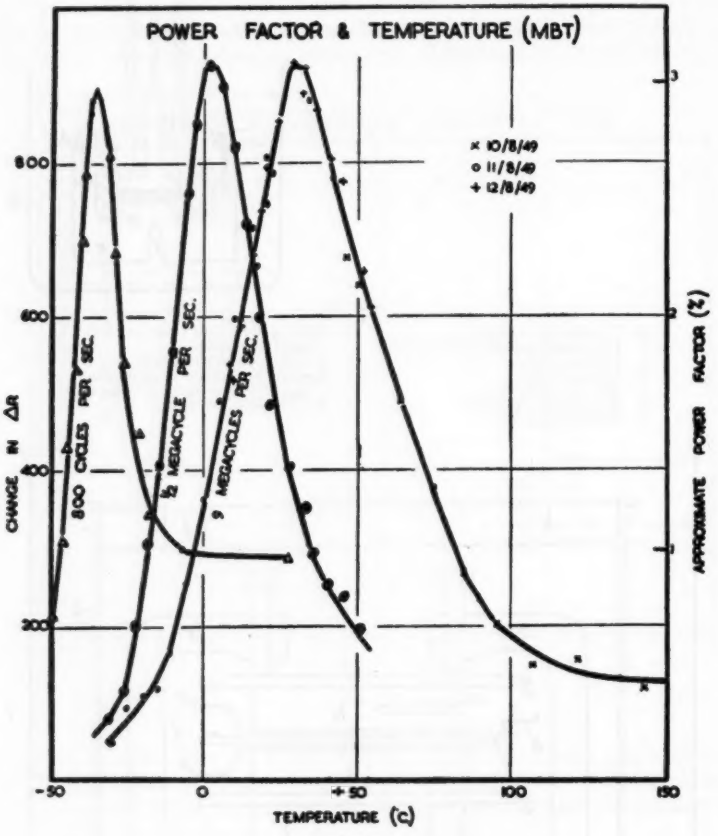

FIG. 16.

slightly lower temperatures. With normal equipment, one will have to remain satisfied, for the present, with studying self-curing systems at laboratory or slightly elevated temperatures.

DISCUSSION AND CONCLUSIONS

Considering the experimental results as a whole, the following points are important, both for practical applications in the factory and for the planning of future research on vulcanization problems.

(1) Changes in electrical power factor can be used to follow the progress of sulfur combination with rubber over a wide range of curing systems. (Fillers with large dielectric loss must not be present.)
(2) Even allowing for experimental error and the problem of temperature control, it is clear that a single correlation curve cannot be used to convert power factor into combined sulfur.
(3) The main outstanding difference in correlation resulted from the presence or absence of zinc oxide in the mix. In every case the omission of zinc oxide produced a curve lying closer to the power factor axis.

On modern theories of vulcanization, as presented by Bloomfield and coworkers[18], it is contended that zinc oxide promotes disulfide linkage, while in its absence monosulfide combination is preferred. If this is the case, fewer links are formed from the same amount of sulfur when zinc oxide is present.

The experimental results on power factor could support this view if it could be shown that the dipole moment contribution to power factor for disulfide links is less than that arising from double the number of monosulfide links. To test this, data were found in the tables of Landolt-Börnstein (Table 9).

TABLE 9

	$\mu \times 10^{-18}$ e.s.u.	Observers
Diphenyl sulfide	1.50	de Vries Rodebush
	1.56	Bergmann Engel Sandor
	1.47	Bergmann Tschudnowsky
Diphenyl disulfide	1.81	Bergmann Tschudnowsky
	1.56	de Vries Rodebush

The agreement for the disulfide was not good, so samples of the corresponding dilauryl compounds were made and tested in the I.C.I. Research Department, Blackley.

	$\mu \times 10^{-18}$ e.s.u.
Dilauryl monosulfide	1.66
Dilauryl disulfide	2.01

According to a formula, due to Sillars[19] and discussed by Oakes and Richards[20], the dipole moment can be calculated from the power factor:

$$\bar{\mu}^2 = \frac{\epsilon \tan \delta \text{ (max.)} \; 27kT}{2\pi \; (\epsilon_0 + 2)^2 n\alpha}$$

where

$\bar{\mu}$ = mean diploe moment.
ϵ = dielectric constant.
$\tan \delta$ (max.) = power factor at maximum absorption.
ϵ_0 = static dielectric constant.
n = number of dipoles per cc. dielectric.

If the data for the dilauryl compounds are used, the power factor contribution is proportional to μ^2, so one gets for monosulfide links 2.76 and for half as many disulfide links 2.02. The ratio of these numbers agrees fairly well with the observed slopes of the correlation curves between combined sulfur and power factor, with and without the addition of zinc oxide.

Alternatively, with the same formula, it is possible to calculate the dipole moment from the power factor data. Assuming monosulfide links in both cases and using a value of $\alpha = 0.6$ one gets:

With zinc oxide 1.39×10^{-18} e.s.u.

Without zinc oxide 1.74

Assuming all disulfide links with zinc oxide present μ is then 1.99.

The results for μ are given in Table 10.

As far as order of magnitude the agreement is good, considering that the power factor data are obtained in rubber and the dipole moment for dilauryl compounds are from experiments on benzene solutions.

In relation to theories of vulcanization, Bloomfield puts forward the idea that reversion consists in —S chains going over to —S in ring structures. If one argues from dipole moments (assuming thiophene with a dipole moment of 0.63 to be typical of S in ring compounds) reversion should result in curvature away from the power factor axis in the graphs relating combined sulfur to power factor. This in fact was the tendency observed when zinc oxide was omitted, though, as pointed out previously, most or all of the curvature of this type could be accounted for by corrections for tan δ (max.) and α but when zinc oxide was present the curvature was usually reduced or even of the opposite sign.

TABLE 10

Type of link	Calculated from power factor data	Observed for dilauryl compounds
Monosulfide	1.74	1.66
Disulfide	1.99	2.01

Much of this reasoning is necessarily speculative, but it helps to show the potentialities of the method. As the catalogue of dipole moments of sulfur compounds is improved, the contribution by each type of link will be known with greater accuracy. Many hypotheses and theories of vulcanization can then be submitted to the test.

Infrared technique has developed along similar lines, and is now well established as a powerful analytical tool.

The study of radio frequency spectra of different curing systems will undoubtedly increase and, in the process, more information will be forthcoming in relation to the problem of vulcanization.

SUMMARY

Over a wide range of curing systems electrical power factor was found to increase as combination with sulfur proceeded. The main experimental results were obtained at nine megacycles frequency and laboratory temperature, using a Q-meter for the electrical measurements.

Some experiments were also carried out through frequency and temperature range.

Analysis of the data shows that no simple conversion factor can change electrical power factor into combined sulfur, indicating that the electrical

losses are affected by the type of combination with sulfur. The omission of zinc oxide causes a marked increase in the rate of change of power factor with combined sulfur.

Dipole moments have been calculated from the slopes of these correlation curves, assuming monosulfide —S— when zinc oxide was not included in the mix and disulfide —S—S— when zinc oxide was present. Reasonable agreement has been obtained with experimental data on simpler compounds, *e.g.*, dilauryl mono- and disulfides.

The experimental technique has provided an analytical tool with possible applications both to problems of factory control of cure and to checking theories of vulcanization.

AKNOWLEDGMENTS

The author is indebted to Mr. Longster for the data and measurements on dipole moments of sulfur compounds, and to Dr. W. J. S. Naunton for his general interest in the investigation.

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DIELECTRIC RELAXATION OF NATURAL RUBBER VULCANIZATES *

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INTRODUCTION

It has been known for a long time that the dielectric behavior of vulcanized rubber is very similar to that of dipolar liquids, and there is little doubt that the dielectric losses and the relatively high permittivity of cured rubbers are due to dipoles which have been formed during vulcanization. Nevertheless, few systematic investigations[1] have been published on the influence of the sulfur content on the dielectric loss, and the effect of different types of cure appears to have been studied mostly at only one or two test frequencies[2]. This practice of confining measurements to a limited frequency range can, of course, give a misleading picture of the dipolar nature of the rubber because comparisons of any two samples may involve different parts of their dispersion curves. We have, therefore, investigated the dielectric losses of four types of vulcanizates over a relatively large frequency range and present the results in this paper.

EXPERIMENTAL

These four different cures were carried out with:

(1) sulfur and no accelerator;
(2) sulfur and tetramethylthiuram disulfide (TMT) as accelerator;
(3) sulfur and zinc diethyldithiocarbamate (ZDC) as accelerator;
(4) tetramethylthiuram disulfide (TMT) and no sulfur.

Uncompounded crepe was also included in these experiments. Formulas and curing times are given in the Appendix. All samples were measured both before and after a 24 hours' extraction with acetone under nitrogen, followed by high-vacuum drying, but only the data for the extracted samples are reproduced, apart from one case which is reported to illustrate the effect of extraction.

The electrical measurements were carried out at the prevailing room temperature, which varied between 15° and 21° C, but was constant for each curve. The frequency range extended from 200 c/s. to 40 Mc/s. Up to 12 kc/s. a Schering Bridge with Wagner earth was used, the samples being discs of 5-inch diameter and $\frac{1}{16}$ inch thick. These samples were cured between stainless steel plates, and it was found that tin-foil electrodes stuck to them very well without adhesives when attached after vulcanization. At radio frequencies, a resonance method was employed, in which the equipment was very similar to the apparatus described in earlier papers[3]. The connections between the sample condenser and the test set were made as short as possible so that their impedance was negligible. Here, the samples measured only 2 inches by 1 inch,

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 27, No. 1, pages 40–48, February 1951.

and no tin-foil electrodes were used because it had been found that, within the limits of experimental error, tin-foil covered and bare samples gave the same results.

RESULTS

The results of the measurements are shown in Figures 1 to 4. The graphs in Figures 1, 2, and 3 are typical dispersion curves, in which the level of the loss tangent increases, and the maxima are displaced towards lower frequencies, as the sulfur content increases. Figure 3 includes the curves for two samples of almost the same sulfur content, but differing in that one of them which is repre-

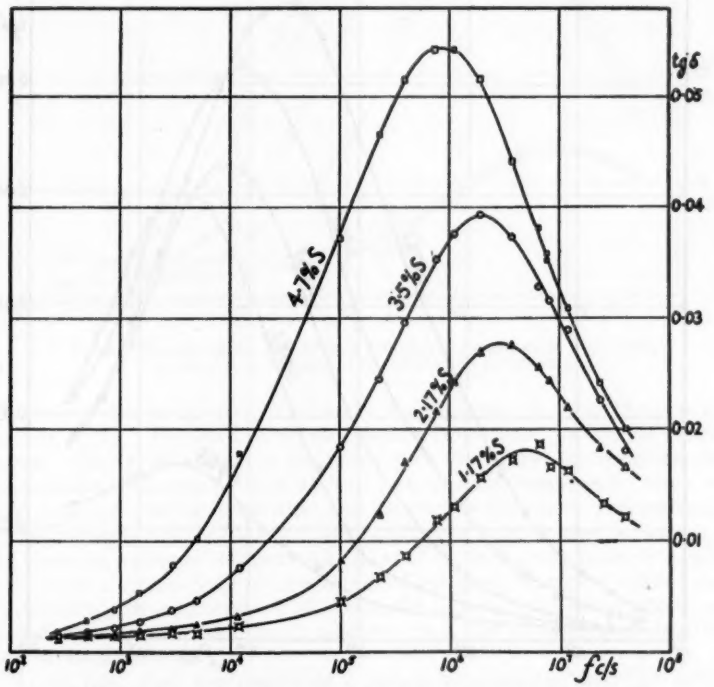

FIG. 1.—Variation of loss tangent with frequency of rubbers cured without accelerator; percentages of combined sulfur as indicated.

sented by the broken line had not been extracted. It will be seen these two curves diverge only at the low frequency end of the graph, where the losses in the unextracted sample are appreciably higher than in the extracted rubber; on the other hand, the high frequency losses are hardly influenced at all by the extraction. This has been the general experience with all vulcanizates.

A sulfurless cure (Figure 4) produces a rubber with very much lower losses at radio frequencies than the more orthodox methods of vulcanization. The losses rise slowly with increasing frequency, but the measurements do not reach sufficiently high frequencies to indicate whether the curve has a definite maximum. The same figure (4) contains the data for extracted and unextracted

crepe. Acetone extraction has a similar effect on crepe as on vulcanized rubber, and here again there is a slow rise of the losses with increasing frequency.

We think that the low-frequency reduction of the loss tangent by acetone extraction is not so much due to the extraction itself as to the subsequent drying. The reason for this assumption is shown by the results in Figure 5, which gives the losses at low frequencies of two differently compounded samples, both in their original state and after drying in a vacuum desiccator over phosphorus pentoxide for about six weeks. The similarity between the effects of acetone

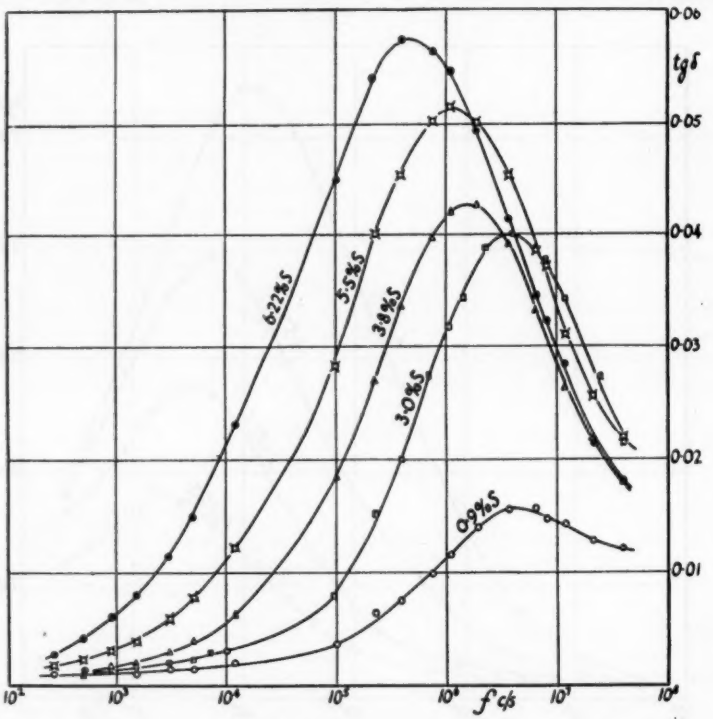

FIG. 2.—Variation of loss tangent with frequency of rubbers cured with TMT as accelerator; percentages of combined sulfur as indicated.

extraction and mere drying is obvious. The initial losses may be expected to depend on the relative humidity at the time of curing.

DISCUSSION

Although the curves in Figures 1 to 3 have the form of typical dielectric dispersion curves, their widths are much larger than is provided for by the well known Debye equations. This is also quite a common occurrence in liquids and is generally interpreted as the result of a distribution of relaxation times. It has been shown[4] that even when the distribution function is not known, it is still possible to calculate the dipole moment, or at least the quantity $N\mu^2$, where

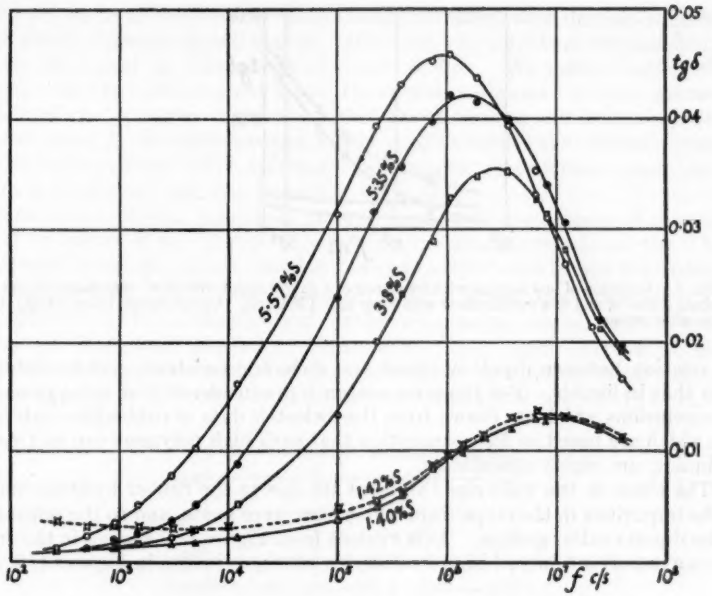

FIG. 3.—Variation of loss tangent with frequency of rubbers cured with ZDC as accelerator; percentages of combined sulfur as indicated.

N is the number of dipoles per cc. and μ their magnitude, from the area under the loss curve. We shall, however, refrain from doing so for the following reasons. The sulfur which is combined with the rubber hydrocarbon during vulcanization is known to form at least two types of compounds; some of the sulfur forms polysulfide cross-links and determines the elastic properties of the rubber, but only a part of the combined sulfur can be accounted for in this way. The chemical evidence[5] suggests that most of the remaining sulfur is combined in the form of heterocyclic groups arranged randomly along the rubber chains. It appears highly improbable that all dipoles have the same magnitude, and a routine calculation of the dipole moment from the experimental data is not likely to be significant.

Apart from this, the results of a recent investigation into the dielectric properties of swollen rubbers[6] suggest that the chain structure of rubbers modifies the dielectric relaxation mechanism, and it is only to be expected that

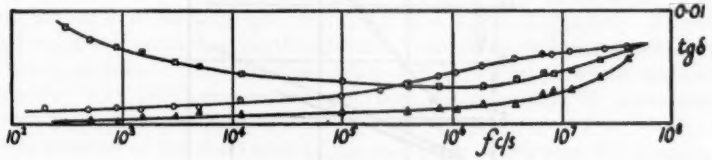

FIG. 4.

FIG. 4.—Variation of loss tangent with frequency of unextracted crepe □, extracted crepe Δ, and of rubber cured with 3 per cent TMT ○.

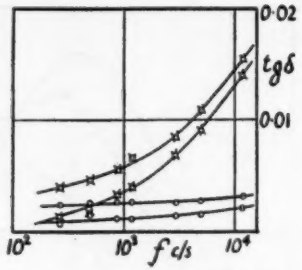

FIG. 5.—Variation of loss tangent with frequency of a rubber cured with ZDC containing 5.7 per cent combined sulfur × and of a rubber cured with 3 per cent TMT (○). Upper curves: before drying; lower curves: after drying.

the relation between dipole moment and dielectric constants will be different from that in liquids. For the same reason it is considered that quite generally all conclusions which are drawn from the dielectric data of rubberlike materials, and which are based on the assumption that such high polymers can be treated as liquids, are highly speculative.

The losses in the vulcanized rubbers are due to the rubber hydrocarbon or to the impurities in the crepe from which they were made, and to the relaxation of the dipolar sulfur groups. As is evident from Figure 4, the losses in the crepe become important only at high frequencies where, as is seen in Figures 1, 2, and

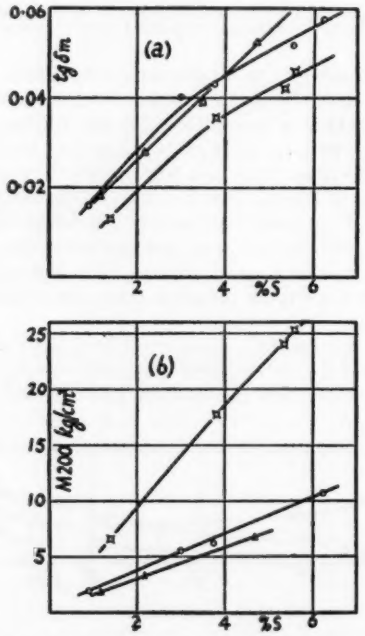

FIG. 6.—Variation of maximum loss tangent $tg\delta_m$ (*a*) and Modulus at 200 per cent elongation *M* 200, (*b*) with percentage combined sulfur. Accelerators: Δ, none; ○, TMT; ×, ZDC.

3, the curves for rubbers which contain little combined sulfur descend somewhat more slowly than one would expect. However, the heights of the maxima are hardly influenced by this source of dielectric loss. We notice further that, except when the sulfur content is low, the curves in Figures 1 to 3 are geometrically similar. It appears, therefore, that the maximum loss tangent $tg\delta_m$ and the frequency f_m at which it occurs can be used to specify the dielectric properties of these rubbers. The maximum loss tangent should bear some relation to the total dipolar material present in the rubber.

The values of $tg\delta_m$ have been plotted against the percentage of combined sulfur in Figure 6(*a*). It will be seen that the unaccelerated and the TMT-accelerated cures give similar results, but that a ZDC cure lowers the dielectric loss significantly. It is interesting to compare these data with the elastic properties of the same samples, and for this purpose the moduli at 200 per cent elongation have been plotted in Figure 6(*b*). Here again there is no great difference between the unaccelerated and the TMT-accelerated cures, but ZDC gives a very much higher modulus for the same amount of combined sulfur.

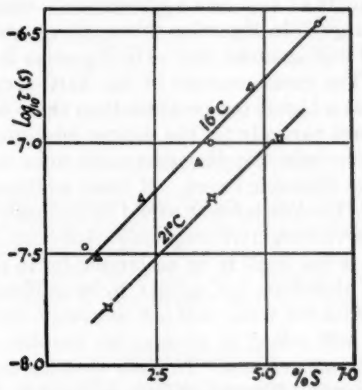

FIG. 7.—Variation of logarithm of relaxation time with percentage combined sulfur. Accelerators: Δ, none; O, TMT; ×, ZDC.

Figure 6 suggests an obvious interpretation when it is recognized that the mobility of a dipole which lies in a cross-link is severally restricted because both ends of it are attached to high polymer chains. It is, therefore, to be expected that dipolar cross-links contribute little to the polarization of the rubber, and that the dielectric losses are predominantly due to sulfur which is not combined in cross-links and which may be called useless sulfur. It follows that, for a given amount of combined sulfur, the dielectric losses decrease with increasing modulus. This is indeed borne out by Figure 6, which also shows graphically how ZDC as accelerator favors the formation of cross-links in preference to other reactions.

The position of the maximum of the loss curves determine the average dielectric relaxation time τ by means of the relation:

$$\tau = 1/2\pi f_m \qquad (1)$$

The relaxation time has a very large negative temperature coefficient, and its temperature dependence can be described, at least within a limited region, by an equation of the type:

$$\tau = \tau_0 e^{E/RT} \quad (2)$$

where E, the so-called activation energy, is generally assumed to be the height of the energy threshold which separates adjacent equilibrium positions and which the dipolar unit must surmount before relaxation can take place[7]. Examples of the temperature dependence of the relaxation time of rubber are given, for instance, by Schallamach and Thirion[6].

As pointed out before, no provision for maintaining constancy of temperature was made in these experiments, but there are for each type of vulcanizate at least three curves which were determined at temperatures not differing by more than 1° C. The logarithms of the corresponding relaxation times have been plotted against the sulfur content in Figure 7. The experimental material is limited for any one type of vulcanizate, but taking the results presented in Figure 7 as a whole there is an indication that the relation between relaxation time and sulfur content is at any rate approximately exponential, suggesting that the activation energy E in Equation 2 is approximately a linear function of the sulfur content if it is assumed that τ_0 in Equation 2 does not depend on the sulfur content[8]. The measurements of the ZDC-accelerated compounds have been carried out at a higher temperature than those on other compounds, and this accounts at least partially for the shorter relaxation times found here.

We should like to conclude this discussion with some remarks on the influence of moisture on the dielectric losses. If these additional losses were only due to ionic conduction, the loss tangent would be inversely proportional to the frequency, but the observed negative frequency coefficient of the low frequency losses in moist rubbers is too small to be accounted for in this way, and simple ionic conduction does, therefore, not appear to be sufficient to explain these losses. It is expected that the water will not be evenly distributed throughout the rubber but that it will collect in microscopic droplets and thus make the rubber dielectrically inhomogeneous. In such systems frequency dependent losses, known as the Maxwell-Wagner effect, are possible, and it is interesting to note that this effect has provided an explanation of the low-frequency losses in carbon-loaded rubbers[9]. In our case, the effect should be enhanced if the water forms solutions of water-soluble impurities such as proteins, and so may well explain the low-frequency losses in moist rubber.

SUMMARY

The dielectric loss tangent of different types of vulcanizates of natural rubber has been measured as function of the frequency. Comparisons of the losses in different vulcanizates containing the same amount of combined sulfur show that they decrease with increasing modulus, and it is suggested that the dielectric loss is mostly due to sulfur which has been combined in forms other than cross-links. The dielectric relaxation time is approximately an exponential function of the percentage of combined sulfur.

It has been found that moisture increases the audiofrequency losses in rubber more than the radiofrequency losses.

APPENDIX

The indicated amounts of vulcanizing ingredients are expressed as parts per 100 parts of crepe.

Combined Sulfur	Compounded Sulfur	Accelerator	Zinc oxide	Stearic acid	Temp. of cure (° C)	Time of cure (min.)
	Fig. 1					
1.17	4	—	—	—	142	60
2.17	6	—	—	—	142	120
3.5	8	—	—	—	142	180
4.7	8	—	—	—	142	180
	Fig. 2					
0.9	1	TMT 0.3	2	—	142	30
3.0	3	0.3	2	—	142	30
3.77	5	0.3	2	—	142	30
5.52	10	0.3	2	—	142	30
6.22	10	0.3	2	—	142	30
	Fig. 3					
1.40	1	ZDC 1	2	0.5	100	60
3.8	4	1	2	0.5	100	60
5.35	7	1	2	0.5	100	60
5.57	7	1	2	0.5	100	60
	Fig. 4					
(0.4)	—	TMT3	2	—	142	30

ACKNOWLEDGMENT

The author wishes to thank the Technological Department of this Association for the preparation of the samples, and the Analytical Department for the sulfur determinations.

The work reported here forms part of a program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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THERMOELASTIC PROPERTIES OF NONCRYSTALLIZING RUBBER *

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In a preceding work on the thermodynamics of rubber[1], it was shown that when the external pressure p in the equation of state of rubber is less than one kg. per sq. cm., the factor involving p may be neglected. In this case the equation of state of rubber may be derived from the following relationships:

$$V_0 f = \left(\frac{\partial U}{\partial \lambda}\right)_{p,T} - T\left(\frac{\partial S}{\partial \lambda}\right)_{p,T} \tag{1}$$

or

$$V_0 f = \left(\frac{\partial U}{\partial \lambda}\right)_{p,T} + T\left(\frac{\partial V_0 f}{\partial T}\right)_{p,\lambda} \tag{2}$$

where U and S are the specific internal energy and entropy; p is the pressure, T is the absolute temperature, $V_0 = V_0(p,T)$ is the specific volume of the rubber in the undeformed state, λ is the relative length, and f is the conditional stress (the tensile or compressive force divided by the initial cross-section of the test-specimen).

During elongation or compression, there are (1) a reorientation of the chain molecules; (2) a change of the mean distances between the atoms and molecules, and (3) deformation of the valence angles. Hence, the deformation of rubber, as demonstrated by Alexandrov and Lazurkin[2], is made up of both elastic and high elastic elements. The value of the elastic element of deformation is usually estimated by comparing the high elastic modulus with the modulus of elasticity of the rubber in a "vitreous" state.

From the measurements of Kobeko and his associates, it follows that the modulus of elasticity of rubber in the "vitreous" state is approximately 2000 times greater than the high elastic modulus (10 kg. per sq. cm). From this it follows that, in the high elastic state, the elastic energy (above the point Tg) resulting from the increase of the mean distances between the units and from the deformation of the valence bonds, constitutes less than 0.05 per cent of the total energy of deformation. Since this energy of elasticity is part of the internal energy of the substance, it would appear possible to ignore the term $\left(\frac{\partial U}{\partial \lambda}\right)_{p,T}$ in Equation (1). However, it is necessary to take into account the fact that the internal energy in the form of potential energy is also a function of the degree of reorientation of the chain molecules. This may be best observed in the case of the crystallization of linear polymers, when the chain molecules pass directly from an unoriented state to a strictly oriented relative distribution. Crystallization, as is well known, leads to a decrease of internal energy.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Colloid Journal*, Vol. 12, No. 4, pages 241–247 (1950).

The same effect, possibly to a lesser degree, takes place in the deformation of an amorphous high elastic material which is not accompanied by the development of a crystalline phase. Consequently, it is impossible to ignore the effect of orientation on the internal energy, and it should be calculated from the term of the relation: $\left(\frac{\partial U}{\partial \lambda}\right)_{p,T} < 0$. This leads to a decrease of f, as is evident from Equation (2), with respect to the value for ideal rubber in which case $\left(\frac{\partial U}{\partial \lambda}\right)_{p,T} = 0$. In the case of an ideal rubber, the internal stress is strictly high elastic, of entropic origin.

It is particularly important to establish the role of internal energy in the deformation of rubber. Attempts to solve this problem by various investigators proved fruitless for a number of reasons. These reasons explain why the method is unsatisfactory and consequently also the choice of the material studied itself (crystallizing rubber).

It is known that vulcanizates of crystallizable rubbers cannot be considered ideal. Hence, it is necessary to select an uncrystallizable rubber. One aim of the present work, in addition to the establishment of the thermoelastic law for vulcanizates of uncrystallizable butadiene-styrene rubber, is an attempt to reach a solution of the question discussed by using an exact method and exact thermodynamic relationships. One of the causes of failure in the work of Meyer and Ferri, and of Anthony, Guth and others is the use of inexact thermodynamic relationships which we noted in a previous work[1].

METHOD AND MEASUREMENTS

As the object of investigation, we chose a Buna-S vulcanizate containing 3 per cent sulfur. The specimens, their preparation, and details of the measurements are described in another of our works[3]. In studying the equilibrium relations f-T at different deformations λ, we selected the method used by Roth and Wood[4] and later defined it more precisely.

As distinguished from the relaxation method of Meyer and Ferri (L = constant), Roth and Wood represented the relative length by a constant (λ = constant). The method consists of heating the stretched specimen up to 70–80° C, at which temperature the relaxation proceeds more rapidly, and then waiting the necessary time (so that the stress may become fixed), and next cooling gradually, since the length of the specimen L may change at a lower temperature so that the relative length $\lambda = \frac{L}{L_0(p,T)}$ remains constant. Here $L_0(p,T)$ is the length of the specimen before deformation with respect to the temperature and pressure. In calculating the tensile force, the only factor taken into account is the time necessary to establish a uniform temperature throughout the test-specimen. The stress in this method of measurement corresponds at any temperature to the relaxed state.

The unsuitability of the l = constant method lies in the necessity of computing the additional relaxation of the stress resulting from the change of λ at lower temperatures.

Since many investigators have demonstrated the approximately linear relation between the stress and temperature for different rubbers (and the present author for the rubber studied between 0 and 80° C), we confined ourselves to a careful measurement of the stress at two different temperatures; *viz.*, room temperature and the maximum temperature.

As a correction of λ = constant, the coefficient of linear expansion of the vulcanizate studied was determined; it was $\beta = 2.1 \times 10^{-4}$ per degree.

If L is the distance between marks made on a uniform area of the deformed test-specimen, the correction for the length (ignoring anisotropy in the thermal expansion) is measured by the formula; $\delta L = L \cdot \beta\theta$, where θ is the difference between the temperatures.

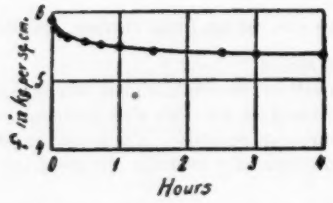

FIG. 1.—Character of stress relaxation of vulcanized butadiene-styrene at 70° C (λ = constant).

To find the maximum temperature attainable in the experiment, the relaxation of stress at different temperatures was studied. It was established that, at 80° C, the relaxation curve tends toward a gradual continuous decrease, evidently as a result of changes in structure of the three-dimensional network of the vulcanizate. At 70° C this phenomenon was not observed. The character of the relaxation curve at this temperature is shown in Figure 1.

From these results we obtained a maximum temperature of 70° C, and a time of relaxation of 2 hours. The results of measurements of a gradually lowering temperature and of a gradually rising temperature are shown in Figure 2. These results show that, even after two hours, relaxation is not complete, and the cyle of cooling and heating leads to an additional decrease of stress at 70° C.

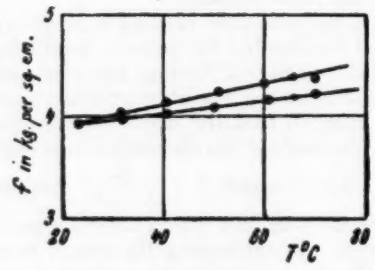

FIG. 2.

Figure 3 shows that only after a few heating and cooling cycles is the balanced stress attained. This method was used in later work.

From the last column of the table it is clear that the discrepancy in the data appears to indicate experimental errors. The mean values in all six measurements show quite clearly that the part played by internal energy in the high elastic deformation of rubber is insignificant. Unfortunately, the accuracy of the experiment does not make it possible to say definitely whether $(dU/d\lambda)_{p,T}$ is a small negative quantity as was expected and obtained in the experiment.

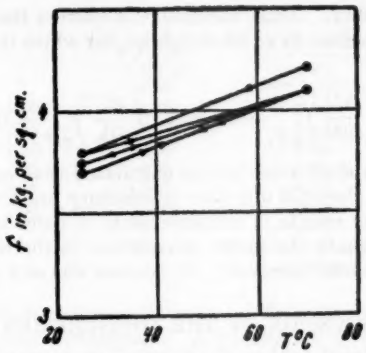

FIG. 3.—Relaxation cycles for vulcanized butadiene-styrene rubber at strain λ.

Ross and Budd in their measurements also obtained a negative value for this term for vulcanized GR-S.

Since the compressibility of rubber does not differ much from that of solid amorphous substances, an actual change in the volume of uncrystallizable rubber under stress should be quite small.

The value may be determined from the following expression for the theory of elasticity:

$$3K = \frac{E}{1 - 2\mu}$$

For vulcanized rubber, the modulus of repeated compression is $K \approx 10^4$ kg. per sq. cm. and the modulus of unilateral strain is $E \approx 10$ kg. per sq. cm. It follows from this that the Poisson coefficient is 0.5 ± 0.03 per cent. This will give, in accordance with the relation: $\log \frac{V}{V_0} = (1 - 2\mu) \log\lambda$, at 300 per cent elongation an increase of volume up to 0.08 per cent. The well known experiments of Holt and McPherson[6] also show that vulcanized rubber up to 300 percent elongation changes its volume less than 0.1 per cent. This, however, does not justify the assumption that the thermodynamic relation (5) in this case will coincide with (1), since, for a 1 per cent volumetric compression of rubber, a

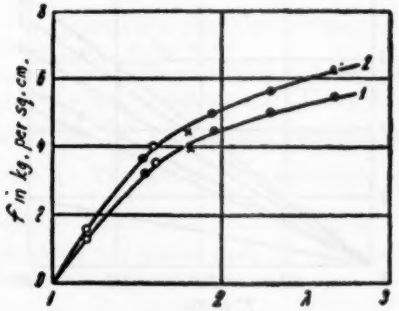

FIG. 4.—Balanced isotherms of strain of vulcanized butadiene-styrene rubber at temperatures: (1) 25° C. (2) 70° C.

high pressure is necessary. Thus, the rubber studied in the present work can be considered to be quite close to an ideal rubber, for which it is necessary to meet these two conditions:

$$\left(\frac{\partial U}{\partial \lambda}\right)_{p,T} = 0 \quad \text{and} \quad \left(\frac{\partial V}{\partial \lambda}\right)_{p,T} = 0$$

Ross and Budd in their experiments calculated that relaxation is complete in 0.5 to 2 hours, but they did not offer satisfactory proof of this.

Figure 4 shows the results of measurements of three test-specimens. The strain isotherms, shown in the figure, correspond to the temperatures 25° and 70° C, and to atmospheric pressure. In no case was any residual deformation observed.

DISCUSSION OF THE MEASUREMENTS

For ideal (vulcanized) rubber, the internal energy and the volume do not depend on the parameter λ. For real rubber, the internal energy and volume are functions of λ. In the thermodynamics of vulcanized rubber, the parameter λ plays the same role as the volume V in the thermodynamics of a gas. For a real gas, subjected to the van der Waals equation, the internal energy and entropy appear thus:

$$U = \psi_1(T) - \frac{a}{V}; \quad S = \psi_2(T) + R \log(V - b)$$

analogously the case of real rubber appears thus:

$$U = U_1(V,T) + U_2(\lambda); \quad S = S_1(V,T) + S_2(\lambda) \tag{3}$$

hence:

$$V = V(p,T,\lambda) \tag{4}$$

Strain in vulcanized rubber takes place when p = constant. In case the experiment had been performed at V = constant, we could have used the following thermodynamic equation:

$$V_0 f = \left(\frac{\partial U}{\partial \lambda}\right)_{V,T} - T\left(\frac{\partial S}{\partial \lambda}\right)_{V,T} \tag{5}$$

where both partial derivatives, as in Equation 3, depend only on λ.

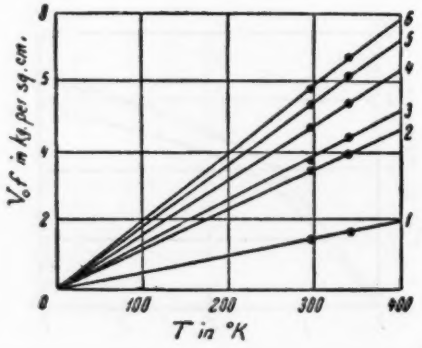

FIG. 5.

TABLE 1

Number of specimen	λ	$V_0 f \times 10^{-6}$ in erg per gram	$(dU/d\lambda)_{p,T}$ (erg per gram $\times 10^6$)	(%)
1	1.20	1.50	−0.04	−3
2	1.55	3.57	0.49	14
1	1.60	3.97	−0.65	−16
2	1.95	4.82	0.06	1
1	2.29	5.95	−0.37	−6
1	2.68	6.06	−0.44	−7
			Mean value	−3%
			Mean deviation	7%

This experiment, unfortunately, is just as difficult as the measurement of the heat capacity C_v of solid substances. A number of investigators, *e.g.*, Guth, Anthony, Peterson, and others, misused equations of type (5), particularly in the evaluation of the role of entropy in the deformation of vulcanized rubbers, since the experiments were performed at constant pressure. In this case it is necessary to use the thermodynamic Equation 1 or 2.

Here, however, the partial derivatives, as is evident from Equations 3 and 4, are functions of the deformation and the temperature.

In the absence of crystallization under strain, the partial derivative, $(\partial S/\partial\lambda)_{p,T}$, hardly seems to be related to the temperature. This follows from the experimentally established linear relation of the stress f to the temperature, as shown by the thermodynamic equation:

$$\left(\frac{\partial S}{\partial \lambda}\right)_{p,T} = -\left(\frac{\partial V_0 f}{\partial T}\right)_{p,\lambda}$$

Furthermore, the term $(\partial U/\partial\lambda)_{p,T}$ must depend only slightly on the temperature, as in the case of amorphous substances. Consequently we may write Equation 1 in the following form:

$$V_0 f = \phi_1(\lambda) + T\phi_2(\lambda) \tag{6}$$

This equation may be regarded as only approximate. Nevertheless, it is interesting to use it in order to obtain information on the role of internal energy in the deformation of rubber. Figure 5 shows the corresponding experimental values for the rubber studied. The specific volume of the butadiene-styrene vulcanizate was 1.05 cc. per gram (according to the data of Guth, James, and Mark for density).

From the curves in Figure 5 it is clear that, within the established limits of deformation (< 170 per cent), $\phi_1(\lambda) = 0$.

Wiegand and Snyder[5] showed the possibility of determining the term exactly. The calculation may be made from Equation 2. Using our experimental data, we measured $V_0 f$ and $\left(\frac{\partial V_0}{\partial T}\right)_{p,\lambda}$ λ for the mean temperature 47.5° C, and substituted it in Equation 2. The results of the calculation are given in Table 1.

COMPARISON WITH THE THEORY OF ELASTICITY

In work cited above[1] it was shown that, for the thermodynamics of ideal rubber, the following equation of state applies:

$$f = \frac{T}{V_0(p,T)}\phi(\lambda)$$

Besides, for a single deformation, the following formula applies: $\sigma = \lambda f(V_0/V)$. Because the change of volume of uncrystallizable vulcanized rubber is far beyond the limits of experimental error, the last formula may be simplified:

$$\sigma = \lambda f$$

where σ is the actual stress. Including this formula we have:

$$\sigma = \frac{T}{V_0(p,T)} \lambda\phi(\lambda) \tag{7}$$

In another work[7] a molecular-kinetic theory of high elastic deformation was developed, and it was shown that, within the broad limits of expansion (up to 400 per cent) for vulcanized rubber, the law of deformation is linear:

$$\sigma = E_\infty(\lambda - 1) \tag{8}$$

where E_∞ signifies the high elastic modulus.

From Equations 7 and 8 it follows that:

$$E_\infty = \text{constant} \frac{T}{V_0(p,T)} \tag{9}$$

From the molecular-kinetic theory at the same time, it follows that:

$$E_\infty = \frac{N_0 kTz}{V_0(p,T)(\lambda_\infty - 3/2)} \tag{10}$$

where N_0 is the number of molecular chains in a unit mass; V_0 is the specific volume; z is the number of segments in a molecular chain; and λ_∞ is the high elastic deformation at $\sigma = \infty$.

Thus the temperature relation, E_∞, following from the theory of elasticity, agrees with Equation 9.

Figure 6 shows the strain curves at 25° and 70° C in the coördinates σ,λ. The expected linear nature of the law of deformation is quite evident.

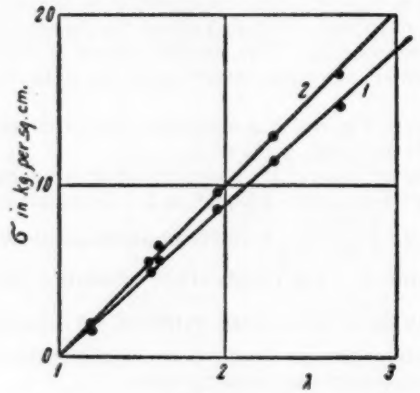

FIG. 6.—Equilibrium curves of strain of vulcanized butadiene-styrene at temperatures: (1) 25° C; (2) 70° C.

From the slope of the curves, the equilibrium high elastic modulus at 25° and 70° C can be calculated. The following results were obtained:

$T°K$	298;	343
E(kg. per sq. cm.)	8.90;	9.95

The ratio of the moduli is 1.118; then as from Equation 9 it follows that:

$$\frac{E_\infty(T)}{E_\infty(T_0)} = \frac{T}{T_0}[1 + 3\beta(T - T_0)]$$

Substituting the corresponding temperature values and coefficient of linear expansion, we obtain a calculated value 1.120.

These results lead to the conclusion that the elastic force, which decreases in the deformation of uncrystallizable (vulcanized) rubber, is of a strictly kinetic nature, as was concluded from our calculation of the law of deformation (8) and the high elastic modulus (10).

CONCLUSIONS

1. A method of measuring and obtaining the equilibrium isotherms of strain for vulcanized butadiene-styrene rubber is described.
2. It is shown that the component of the elastic force of the rubber which depends on the internal energy has a value of several per cent.
3. Calculation shows that the change in the volume of uncrystallizable rubber, at 300 per cent strain, has a value less than 0.1 per cent.
4. A comparison of the results obtained with the thermodynamic equations shows that the deformation of the rubber investigated can be considered strictly high elastic and entropic.
5. A comparison of the experimental data with the theory of high elastic deformation confirms the accuracy of the conclusions from the theory.

ACKNOWLEDGMENT

Engineer-Technologist A. Vishnitskaya participated in the experimental part of the work.

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THE ROLE OF INTERMOLECULAR FORCES IN THE MECHANISM OF HIGH-ELASTIC DEFORMATION. I. THE MOLECULAR MECHANISM AND AN EQUATION FOR THE KINETICS OF HIGH ELASTIC DEFORMATION *

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The kinetic theory of rubber elasticity, which is based on statistical mechanical studies of an ideal structural model, does not explain the reaction between molecular chains independent of the forces of the main chains. This theory, which is the first step in any thermodynamic investigation of high elastic deformation, does not, however, explain the mechanical behavior of true polymers, and the question concerning which factors govern the temperature limits of elasticity remains unanswered.

The thermodynamic method is by its very nature very unsatisfactory as a means of investigation of the elastic properties of true polymers, since, by deformation of similar systems, a state of equilibrium (the subject of thermodynamic investigations) is established only gradually, and the time is sometimes so long that ordinary conditions of equilibrium are never achieved.

Thus the rate at which equilibrium is reached (the subject of investigations of the kinetics of high elastic deformation) is found to be in many cases characteristic of a polymer, whereas the thermodynamic characteristics of equilibrium affect only the border conditions.

The kinetics of high elastic states of deformation, which is an independent and extremely important branch of the science of polymers, has been developed most extensively in recent years in the work of Kobeko, Kufshinskiĭ, and Gubevich[1]; Alexandrov and Lazurkin[2]; Slonimskiĭ and Kargin[3], and others. In these works in particular, the relation between the kinetic characteristics of a polymer and the temperature range of its elasticity were established. The investigations showed that one of the basic problems encountered in trying to explain various theories concerning the molecular mechanism of the deformation of polymers is the problem of the nature of the reaction between molecules and the role in this reaction in high elastic deformation.

Although the concepts developed in the works cited furnish a general insight into the character of this fundamental relationship, they are not sufficient for a thorough understanding of the molecular mechanism, and are even less satisfactory for the development of a corresponding quantitative theory. The present work is an attempt at a more detailed study of the role of intermolecular forces in high elastic deformations. The quantitative analysis of the experimental data is based on the application of the kinetic equation derived in this work.

* Translated for Rubber Chemistry and Technology by Alan Davis from *Colloid Journal*, Vol. XI, No. 5, pages 314-321 (1949).

THE MOLECULAR MECHANISM OF HIGH ELASTIC DEFORMATION

As Alexandrov has several times demonstrated[4], the elastic force involved in the deformation of materials is a consequence of the disruption of the distribution pattern of the structural elements of the system. The process of restoration of this pattern, which takes place by means of heat transfer of the structural elements in the deformed material, constitutes relaxation[5]. Disruption of equilibrium in the next order of elongation is the universal mechanism of elasticity of amorphous as well as of crystalline low-molecular systems. In the case of polymers, besides the mechanism referred to causing elastic properties in the amorphous state, the phenomenon of "high elasticity", which is related to a disruption of the balanced configurations of the molecular chains or, in other words, to deformation of the chain molecules, is a characteristic property. Here, in the ideal case, the balanced distribution in the next order is not upset.

High elasticity, which is a feature of polymeric materials having rubberlike properties, is characterized by a low modulus (in 3 or 4 orders of elongation it is lower than the modulus of elasticity of polymers in the amorphous state), and large temporary deformations are reached. The fact that, even with the very rapid deformation with the particular apparatus employed (a range of 1000 cycles per minute), the modulus maintains its characteristically low value, indicates that the relaxation process, which is related directly to the restoration of equilibrium in the next order, progresses in the temperature range of the high elastic state of the polymer so rapidly that it is hardly detectable[6].

On the other hand, in the deformation of polymers in a high-elastic state of the order of that cited, delayed relaxation also takes place, as is manifest under these conditions in equilibrium being established between deformation and stress in a period of time measured in minutes and seconds.

This phenomenon of slow relaxation, which is characteristic of polymers in a high elastic state, is readily explained if such a state is regarded as a process of partial restoration of balanced configurations of the molecular chains. Clearly under these conditions of deformation, such a process involves the displacement of macromolecules or their segments; on the other hand, the rate of the relaxation process is determined by the probability of such changes.

If the polymeric material is considered to be a spatial network composed of chain molecules, then the rate of the process will obviously be determined primarily by the stability of the intermolecular bonds which impede any internal transformation. Evidently the non-relaxing or equilibrium factor of the stress at high elastic deformation is determined by the presence of stable chemical bonds, which are similar to the cross-linkages in vulcanized rubber. On the other hand, the presence of double bonds (originating in a van der Waals reaction) makes possible a partial restoration of the balanced configurations of the chains rather than a regrouping of these chains.

From this we may proceed to the demonstration that the phenomenon of slow relaxation which is characteristic of high elastic polymers is a process of partial or complete restoration (depending on the development of side chains in the molecular structure formed in the chains of greater valence) of the balanced configurations of the molecular chains; and the rate of this process is determined chiefly by the character of the intermolecular forces in the polymer.

The work of Zubov, Zhurkina, and Kargin[7], which showed that the relaxation processes under conditions of high elasticity are not manifest in systems in which the intermolecular activity of the chains decreases sharply, confirms the assumptions made above.

With respect to intramolecular activity, which involves the reaction between the substituents in adjacent atoms of the chain at temperatures characteristic of the high elastic state of the polymer, the corresponding effects can be observed at very high rates of deformation which are not usually attained in the laboratory.

APPROXIMATE EQUATION OF THE KINETICS OF HIGH ELASTIC DEFORMATION

The hypotheses just evolved make it possible to define in an approximate way the kinetics of high elastic deformations with the aid of the differential equation:

$$\frac{d(\sigma = \sigma_{\sim})}{dt} = (E'_0 - E_{\sim}) \frac{d\epsilon}{dt} - \frac{\sigma - \sigma_{\sim}}{\tau} \qquad (1)$$

which is the simplest generalization of Maxwell's well-known equation[8]. Here σ is the normal stress; $\sigma_{\sim}$ is the equilibrium stress; t is the time; and τ is the time of relaxation.

Equation (1) differs from Maxwell's equation not alone by the substitution of the normal stress σ for its unbalanced component $(\sigma - \sigma_{\sim})$; an equally essential distinction is that here, instead of the modulus of elasticity E_0 of Maxwell's equation, the quantity $(E'_0 - E_{\sim})$ is introduced (designated as E_1), which has an entirely different meaning and order of values. Here E'_0 is the initial modulus and $E_{\sim}$ the "equilibrium modulus", which is characteristic of the deformation of high elastic polymers. Equation (1) describes adequately the process of reversible deformation, which is complicated by the relaxation process, which itself is involved in the transformation of the practically instantaneous high-elastic deformation, designated by the modulus E'_0, into a "balanced" high-elastic deformation, designated by the modulus $E_{\sim}$. With respect to Equation (1), it is necessary to consider merely approximations which are accurate within the limits of the temperature, the rates of deformation, and the times of observation, where (1) the modulus E'_0 retains a characteristically low value, indicating a relative slowing down of the process (ignored here) of restoration of equilibrium in the next order, and (2) there is no rupture of the chemical bonds, which would induce a permanent change of structure as a result of deformation.

As one of the authors has shown[9], the law of equilibrium of the high-elastic deformation of noncrystallizing polymers at low or moderate elongations is linear, and may be written:

$$\sigma_{\sim} = E_{\sim} \cdot \epsilon \qquad (2)$$

Assuming that the law of instantaneous high-elastic deformation is represented by Equation (2), E'_0 may be regarded as practically constant, *i.e.*, it is independent of the deformation and stress.

Equation (1) contains qualitatively all the factors involved in high-elastic deformation. The specific equations which represent the particular case of the mechanical behavior of high-elastic polymers may be derived from Equation (1) and from the conditions determining the field of deformations studied. Thus, deformation at a constant rate: $d\sigma/(d_t) = \text{const} = v$ is defined approximately by the differential equation:

$$\frac{d\sigma}{d\epsilon} = E'_0 - \frac{\sigma - E_{\sim}\epsilon}{\tau v} \qquad (3)$$

which is derived by simple transformation of Equation (1).

Equation (3) is interesting because it makes possible a direct determination of the modulus E'_0 as the tangent of the angle of inclination of the deformation curve when the stress $\epsilon = 0$. Actually, when $\epsilon \to 0$ and $\sigma \to 0$ the second factor in the right hand part of Equation (3) becomes zero, and we have:

$$\left(\frac{d\sigma}{d\epsilon}\right)_{\epsilon=0} = E'_0 \tag{4}$$

Creep, which is determined by the condition: σ = constant = σ_0, is expressed by the equation:

$$\frac{d\epsilon}{d_t} = \frac{\sigma_0 - E_{\sim}\epsilon}{E'_0 \cdot \tau} \tag{5}$$

which is also derived directly from Equation (1) and the condition: $d\sigma/(dt) = 0$. As has already been shown, Equation (1) is valid only as a qualitative expression of the relaxation process of high-elastic deformation.

Progress toward a quantitative representation depends primarily on the necessary clarification of the problem of the relation of the time of relaxation τ to the stress.

TIME OF RELAXATION AS A FUNCTION OF THE STRESS

The possibility that the time of relaxation may depend on the stress was first pointed out by Maxwell[5]. A similar hypothesis, which is applicable to the deformation of polymers, was outlined by Alexandrov[4]. In a recently published work of Gurevich, the following expression for this relation was proposed:

$$\tau = \tau_0 e^{\frac{U_0 - a\sigma}{kT}} \tag{6}$$

where τ_0 and a are constants (independent of stress and temperature); U_0 is the energy of activation of the relaxation process; k is the Boltzman constant, and T is the absolute temperature.

Considering Maxwell's equation and Equation (6) together as a universal law of deformation, the present authors have introduced some interesting experimental material in connection with their data on polycrystals and plastics.

A general idea of the relation between the time of relaxation and the stress evidently is of profound significance, and deserves careful attention. However, Equation (6) appears unacceptable. Actually the inaccuracy of (6) means that, in the case of deformation, the change in the direction of the force must change the numerical value of the time of relaxation, and this is obviously contradictory to the experimental results.

Here an attempt to derive the relation between the time of relaxation and the stress was made by studying the relaxation process at a constant given deformation. In this case, assuming that ϵ = constant, and designating the unbalanced stress $(\sigma - \sigma_{\sim})$ as σ_1, we have from Equation (1):

$$\frac{d\sigma_1}{dt} = \frac{1}{\tau}\sigma_1 \tag{7}$$

Equation (7) conforms to the kinetic equation of reactions of the first order, although τ appears as the reciprocal of the constant of the rate of the process concerned. In the general case, the following equation expresses accurately the relation between the time of relaxation and the temperature:

$$\tau = \tau_0 \cdot e^{\frac{U}{kT}} \tag{8}$$

This equation is analogous to the equation of Arrhenius, and has been widely used in many investigations of polymers. It is absolutely necessary that the transformation of energy of the initial state in the course of the process be limited by the change of the number of elements under stress while the stress remains constant, if Equation (8) is to be applicable to cases of relaxation of stress. Only then is the energy of activation a constant quantity which does not change during the relaxation process.

Proceeding from the assumptions above concerning the process under investigation, it may be easily proved that this requirement is not fulfilled. In fact, in the case considered, the relaxation of stress must be regarded as a combination of two processes: (1) a selective process of regrouping, which causes a sharp decline in stress in the different structural units of the chains, and (2) continued equalization of the stress as a consequence of mechanical reaction between the units.

The latter process means that the energy of activation U in Equation (8), which may be regarded as the difference between the energies of the active and initial states, changes during relaxation to the variable quantity U_0, corresponding to the equilibrium established. The change in energy of activation U, which is equal or opposite according to the sign, to the change of energy from the initial state, is determined approximately by the energy consumed in the course of the process and, in general, is equal to the decrease in the unbalanced energy of elasticity. This may be written in the form:

$$dU = - dW \tag{9}$$

where W is the unbalanced element of the energy of elasticity with respect to the kinetic factor in the relaxation process investigated.

It is quite obvious that the application of Equation (7) to the kinetics of relaxation of the unbalanced stress involves not all the energy of elasticity, but only its unbalanced component. By integrating Equation (9), we obtain, by substitution of the corresponding limits:

$$U_0 - U = \int_0^{\sigma_1} dW \tag{10}$$

Expressing the intensity of the unbalanced energy of elasticity by the equation:

$$W = \frac{\sigma_1^2}{2E_1} \tag{11}$$

and expressing the *kinetic unit of relaxation* by V, we get from Equations (10) and (11):

$$U = U_0 - \frac{V\sigma_1^2}{2E_1} \tag{12}$$

Now, utilizing Equation (8), we finally obtain the relation between the time of relaxation and the stress:

$$\tau = \tau_0 \cdot e^{\frac{U_0 - \frac{V}{2E_1}\sigma_1^2}{kT}} \tag{13}$$

In the equation which has been derived, as distinguished from Equation (6) proposed by Gurevich[10], the time of relaxation is an exact function of the stress, and is free of the discrepancies which rendered Equation (6) inapplicable.

Moreover, instead of the empirical constant a of Equation (6), the coefficient σ_1^2 has here a definite physical meaning. Of particular interest is the fact that Equation (13) includes the kinetic unit of relaxation, without which the concept of activation energy would still be meaningless, because of the unknown value of the structural element to which this quantity refers. An investigation of Equation (13) as a complement to Equation (1) makes it possible to define quantitatively the relaxation process in the high-elastic deformation of polymers.

It should be noted that Equation (13) contains two constants, U_0 and V, relating the mechanical properties of the polymer to its physical structure and, consequently, the equation offers certain possibilities with respect to the characteristic structural properties of the polymers studied.

EXPERIMENTAL VERIFICATION

The experimental verification of the applicability of Equations (1) and (13) may be made most conveniently by a study of the relaxation of stress for a given deformation. In this case it is necessary to use Equations (7) and (13). The differential equation obtained by substitution of (13) in (7) is not important in its final form. Using a series transformation, it is possible to achieve any degree of accuracy desired. However, for the experimental verification of the theory, the differential law was used in the present work, following the method of finite differences in the analysis of the experimental curves. Thus we verified the applicability of the hypotheses developed here in the case of certain rubberlike polymers, since the relaxation of stress was investigated at different temperatures and elongations. The experimental data given below serve to illustrate the method used.

Figure 1 shows the characteristic curve of relaxation of stress for natural rubber (smoked sheet), which was examined in the form of films prepared on cellophane by the evaporation from benzene solutions.

From Equation (7) we have:

$$-\tau \simeq \frac{\Delta t}{\Delta \sigma}(\sigma - \sigma_\sim) \tag{14}$$

The value of the equilibrium stress $\sigma_\sim$ was determined by a method similar to that of Meyer and Ferri[11]. For unvulcanized films of smoked sheet, the equilibrium stress was nearly zero.

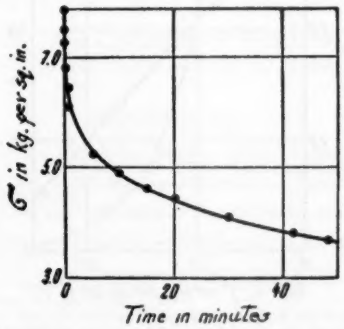

FIG. 1.—Stress relaxation in a film of smoked sheet elongated 100 per cent at 22° C.

Knowing $\sigma_{\sim}$, it is possible, from the curve in Figure 1, to determine the instantaneous values τ at the different points corresponding to the various values of the unbalanced component of the stress.

CHANGE IN RELAXATION TIME τ DURING THE RELAXATION OF STRESS. FILM OF NATURAL RUBBER (SMOKED SHEET)
Pressure 100% Temperature 22° C

t	$\sigma - \sigma_{\sim}$	$-\frac{\Delta t}{\Delta \sigma}$	τ	$\log\tau$
10 seconds	7.0	0.5	3.5	0.542
1 minute	6.0	2.86	17.16	1.234
8 minutes	5.0	12.5	62.5	1.796
32 minutes	4.0	40.0	160.0	2.204

From the data in the table, it is evident that these values change during the process. Furthermore, the accuracy of Equation (13) may be proved by using these experimental values of τ with respect to $(\sigma - \sigma_{\sim})^2$. Here it is expedient to use a semilogarithmic scale, since the logarithmic equation (13) gives the expression:

$$\log\tau = \log\tau_0 + \frac{U_0}{2.3kT} - \frac{V(\sigma - \sigma_{\sim})^2}{(2.3)(2)E_1kT} \tag{15}$$

where $\log\tau$ is a linear function of $(\sigma - \sigma_{\sim})^2$.

From Figure 2 it is evident that the values of $\log\tau$, obtained experimentally, which are plotted against $(\sigma - \sigma_{\sim})^2$, actually fall quite satisfactorily on the curve.

Figure 3 shows a set of experimental curves obtained for natural rubber, where the relaxation of stress was studied at different temperatures.

Instead of undertaking in this work to describe in detail and to interpret the experimental data, we have limited ourselves to the observation that the experimental material relating to different rubberlike polymers confirms beyond

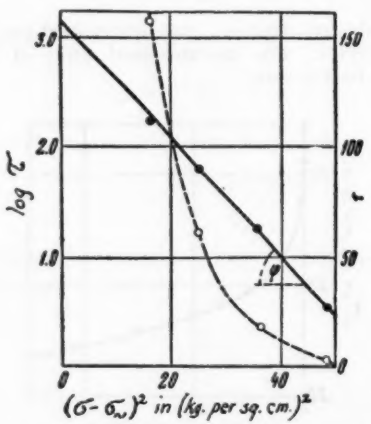

FIG. 2.—Relation between the time of relaxation and the square of the unbalanced stress in simple (dotted line) and semilog (continuous line) coordinates.

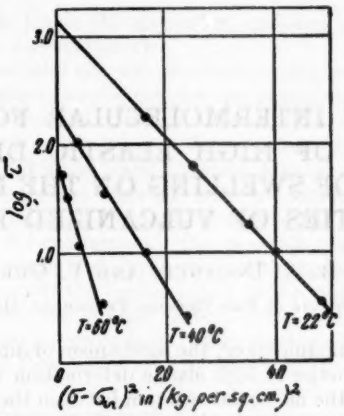

FIG. 3.—Relation between relaxation and square of unbalanced stress. (Smoked sheet; Elongation 100 per cent).

question the applicability of the equations proposed for a quantitative definition of the relaxation process.

SUMMARY

1. The molecular mechanism of the relaxation of deformation of high-elastic polymers has been studied.

2. It is shown that the slow relaxation, which is typical of high-elastic polymers, may be best explained as a restoration process, which either partial or complete (depending on the degree of development of side chains in the molecular structure formed by the main valence chains) of the balanced configurations of the molecular chains.

3. It is shown that the rate of the relaxation process in this case is determined by the molecular activity of the particular polymer.

4. An approximate equation for the kinetics of high-elastic deformation[1] which expresses qualitatively the mechanical properties of high-elastic polymers is proposed.

5. Hypotheses concerning the relation between the time of relaxation and the unbalanced stress are advanced. Equation (2) is derived as characteristic of this relation.

6. It is shown that the joint application of Equations (1) and (2) makes it possible to describe qualitatively the relaxation of stress at constant deformation.

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THE ROLE OF INTERMOLECULAR FORCES IN THE MECHANISM OF HIGH ELASTIC DEFORMATION. III. EFFECT OF SWELLING ON THE MECHANICAL PROPERTIES OF VULCANIZED RUBBER *

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In a preceding communication[1], the mechanism of intermolecular forces was described, and the kinetics of high elastic deformation was discussed, but the quite essential role of the molecular reaction between the chains of the polymer was not discussed. It was shown that the effect of slow relaxation, which is characteristic of high elastic deformation, is a process of partial or complete restoration of the balanced configurations of the molecular chains, and its rate is determined primarily by the intensity of the molecular reaction. Such a theory was then used as a means of developing an equation of the kinetics of high elastic deformation, and of deriving an analytical relation between the time of relaxation and the stress of the deformed specimen. The relation was verified experimentally for polymers of identical structure (in the sense of the size and configuration of the chains) containing different polar groups, which greatly influence the intermolecular forces.

Another effect of the intermolecular forces on the mechanical properties of polymers was disclosed in a study of polymers in the swollen state, for the swelling process, which is not influenced by the molecular structure of the polymer, brings about an essential change in the intermolecular energy[2].

A systematic investigation of the effect of swelling on the mechanical properties of vulcanized rubber, particularly on the kinetics of high elastic deformation, has not heretofore been carried out. We were thus confronted first of all with the development of a suitable method.

APPARATUS AND EXPERIMENTAL METHOD

In experiments on the swelling of rubber in weak solvents, as most frequently performed, the ingredients are separated out of the mixture. To avoid these effects in our experiments, test-specimens of vulcanized rubber were swollen, and the mechanical measurements were made in the vapors of the solvents. To this end an apparatus (elastometer) was constructed, which fulfilled the requirements of the experiment described in the present communication. A schematic diagram of this apparatus is shown in Figure 1.

In a cylindrical glass vessel A with double walls (the jacket of the apparatus) is placed a steel guiding prism on which a small carriage with weights G slides freely. The test-specimen is compressed or stretched in clamps, one of which is fastened to the carriage with the weights G, the other to the upper end of the vessel V. A definite slope of the vessel A corresponds to a definite deforming force acting on the test-specimen. Deformation of the test-specimen was

* Translanted for Rubber Chemistry and Technology by Alan Davis from *Colloid Journal*, Vol. 12, No. 3, pages 184–193 (1950).

measured on a scale B, inside the apparatus, and was viewed through a telescope equipped with a micrometer D.

The micrometer was used also for measuring spring weights placed in vessel A to determine the degree of swelling of the test-specimen of vulcanized rubber. The specimen to be deformed rests on scale E, calibrated in grams. The jacket of the apparatus is equipped with a thermometer. Cock-valves are located on the upper and lower walls of vessel A to release the vapors of the solvent. The model apparatus described assures a sensitivity of 10 milligrams per 250 grams of deforming load. Deformation of the specimen is measured within an accuracy of 0.1 millimeter. The movable part of the apparatus is connected with a kymograph (not shown; behind the apparatus in the diagram), which automatically records the loads applied to the test-specimen during the experiment. To prevent the swollen test-specimen from slipping out of the clamps and thereby disproportionately redistributing the stress, ring-shaped specimens are used, and these are placed in clamps in the cover and carriage.

FIG. 1.—Apparatus for studying the mechanical properties of high elastic substances, as explained in the text.

With this apparatus[3] it is possible to measure the deformation characteristics of high elastic substances. The relaxation of stress of a swollen vulcanizate was measured in the apparatus in the following way. After test-specimens of the vulcanizate were fastened in the clamps and in the spring weights, the small carriage with the weights was fastened with a hook, and the cylinder A was placed in a vertical position. Vapors of the solvent were then passed through the apparatus, and the degree of swelling of the test-specimen was measured by the spring weights. When equilibrium of swelling was reached, cylinder A was in a horizontal position, and the carriage was released from the hook. The deformation of the test-specimen was then measured by the inclination of cylinder A; the constancy of the deformation was established by

the decrease in the angle of inclination of the cylinder. The relaxation of stress was determined by the change on scale F with time.

The concentration of vapors of solvent in the apparatus, which determines the degree of swelling of the test-specimen, was regulated by an apparatus shown in Figure 2. Nitrogen from flash A was passed through a reducer and a tube connected with the pressure regulator RD by two branches. In one of these, the nitrogen passed first through a rheometer R_1, where the rate of flow of the gas was measured, and then the nitrogen passed through a calcium chloride tube X and a spiral tube C. A thermometer was immersed in the solvent which surrounds the coil. From the coil the nitrogen passed into a bubbler B, where it passed through the solvent.

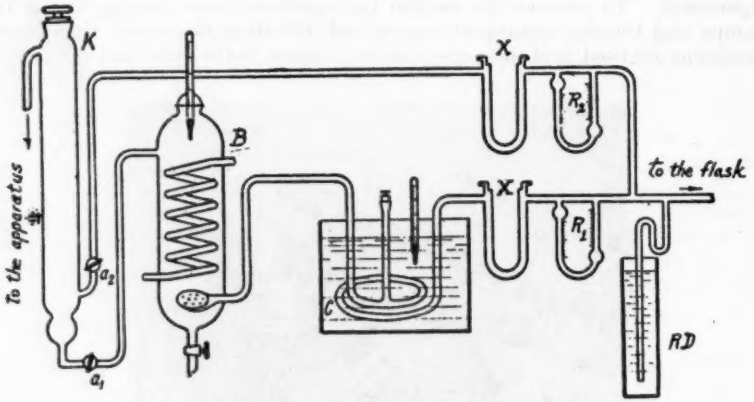

FIG. 2.—Schematic diagram of the apparatus for obtaining the solvent in vapor form, as explained in the text.

From the bubbler the nitrogen, saturated with vapors of the solvent, entered a flask K, filled with broken glass. From flask K the nitrogen passed through a rheometer R_2, and calcium chloride tube X, which was not saturated with vapors of the solvent. Control by stopcocks a_1 and a_2 of the rates of inflow of unsaturated and saturated nitrogen made it possible to change the concentration of solvent vapors in the nitrogen admitted into the main apparatus.

EFFECT OF SWELLING ON RELAXATION OF STRESS OF VULCANIZED RUBBER

The curves of stress relaxation at 200 per cent deformation for specimens of vulcanized natural and polychloroprene rubbers swollen in chloroform vapor or benzene vapor do not differ appreciably from the corresponding curves of the unswollen rubbers [Figure 3]. A deviation from the relationship between the stress σ at a given deformation with the degree of swelling v, having, according to Flory and Rehner[4], the following form, was observed:

$$\sigma = \frac{\rho RT}{M_c}\left(\alpha - \frac{1}{\alpha^2}\right) \qquad (1)$$

This deviation can be explained by the variation in the mean value of the molecular weight of the segments of the chain molecules included between two

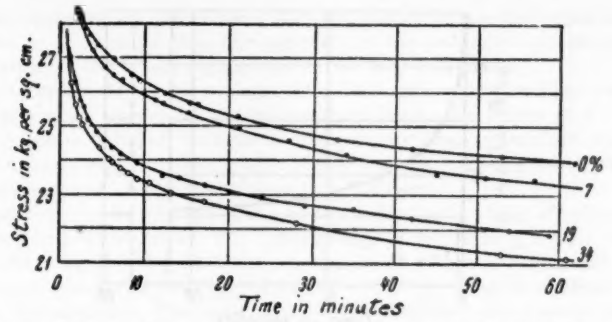

FIG. 3.—Relaxation of stress of vulcanized polychloroprene. Swelling in chloroform.

adjoining bonds of the spatial network of the high ploymer. A part of the bonds of the spatial network is governed by the intermolecular activity of the atoms in the groups. When rubber reacts with molecules of the solvent, partial destruction of the intermolecular bonds takes place. With very high swelling by a solvent, all the bonds of the three-dimensional network are destroyed. Thus, among other things is explained the fact that the properties of greatly swollen vulcanized rubber are better described by a statistical theory.

As a typical application of Equation (1), the molecular weights of segments located between the bonds of the structural network at different degrees of swelling and deformation up to 200 per cent were calculated. The results obtained are shown in Figure 4. Evidently as the degree of swelling increases, the length of the molecular chain segment between the bonds increases, and approaches a constant value.

To describe quantitatively the effect of swelling on the kinetics of high elastic deformations, an equation proposed by Dogadkin, Bartenev, and Reznikovskiĭ was used, which gives the time of relaxation as a function of the stress.

$$\log\tau = \log\tau_0 + \frac{u_0}{2.3kT} - \frac{V(\sigma - \sigma_\sim)^2}{2.3(2E_1kT)} \qquad (2)$$

where τ is the momentary value of the relaxation time, corresponding to the different values of the unbalanced stress, σ is the momentary stress observed for a given moment of the relaxation process; $\sigma_\sim$ is the equilibrium stress; u_0 is the activating energy of the relaxation process; V is the kinetic unit of relaxa-

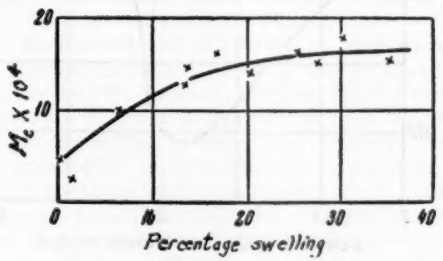

FIG. 4.—Relation of molecular weight of segments of chains between bonds of a vulcanizate to degree of swelling.

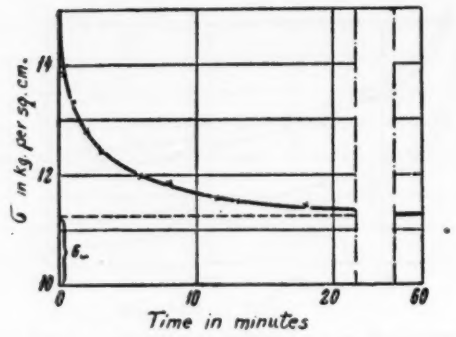

FIG. 5.—Determination of equilibrium stress σ.

tion, and E_1 is the unbalanced high elastic modulus. On a semilogarithmic scale, log τ is a linear function of $(\sigma - \sigma_\sim)^2$. By extrapolating the line log $\tau = f(\sigma - \sigma_\sim)^2$, drawn from the experimental data up to the intersection with the ordinate axis, it is possible to find a definite value when $(\sigma - \sigma_\sim)^2 = 0$. This value for the relaxation time τ^* is a constant, which depends on the relaxation characteristics of the material.

In Equation (2), the instantaneous value of the time of relaxation τ, the momentary stress σ, and the equilibrium stress, $\sigma_\sim$, are all experimentally determined quantities. In agreement with the authors cited above[1], in the case of relaxation of stress:

$$-\tau \approx \frac{\Delta t}{\Delta \sigma}(\sigma - \sigma_\sim)$$

Hence, to determine τ, it is necessary to know the value of the equilibrium stress $\sigma_\sim$. The method of Meyer and Ferri[5] could not be used, inasmuch as heating the swollen vulcanizates higher than the experimental temperature changes the degree of swelling. For this reason $\sigma_\sim$ was determined by extrapolating the linear segments of the relaxation curves (Figure 5) to the intersection of the stress axis. Assuming that the linear parts of the curves of re-

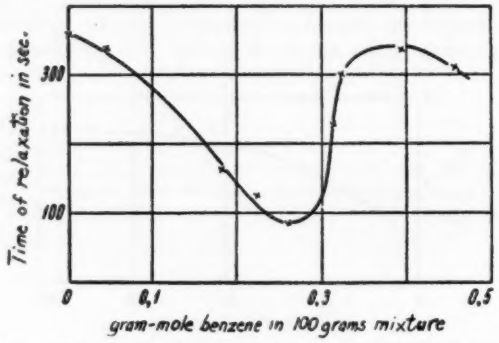

FIG. 6.—Relation of maximum time of relaxation of vulcanized natural rubber to degree of swelling benzene at 29° C.

laxation represent the permanent structural changes in the vulcanizate, *i.e.*, aging, we shall consider that the segment on the ordinate axis cut off by the continuation of the linear segment gives the true value of $\sigma_{\sim}$.

The values of $\Delta t/\Delta\sigma$ were found from the angle of inclination of a tangent for the relaxation curves at points corresponding to the values of σ.

The extreme value of the time of relaxation τ^* was determined for vulcanizates of natural and polychloroprene rubbers at different degrees of swelling in polar (chloroform) and nonpolar (benzene) solvents.

Figure 6 shows the change of this constant for the swelling of natural rubber vulcanized in benzene at 24° C. This change is represented by a complicated curve. At first, swelling causes a decrease of the time of relaxation observed to the point where the swelling reaches $Q = 0.26$ gram-mole of benzene in 100 grams of vulcanizate. The maximum swelling increases the time of relaxation; however, after 100 grams of vulcanizate has absorbed 36 gram-moles of benzene, there is a renewed decrease of the maximum time of relaxation.

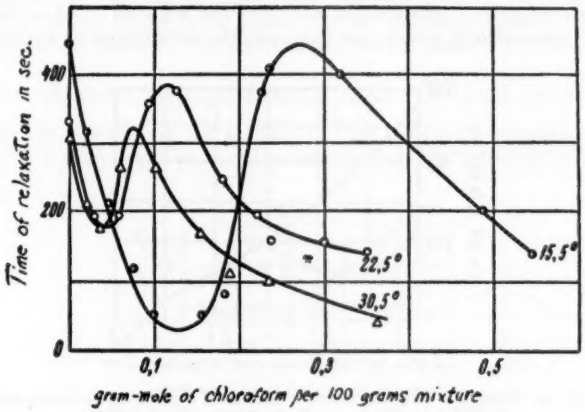

FIG. 7.—Relation of maximum time of relaxation of vulcanized natural rubber to degree of swelling in chloroform at different temperatures.

Similar curves were obtained at experimental temperatures of 30° and 60° C. The relation between the time of relaxation and the degree of swelling of natural rubber in chloroform (Figure 7) at 20.5° C has a similar form. The initial decrease of the time of relaxation ceases when $Q = 0.4$ gram-mole in 100 grams of mixture. The increase of the time of relaxation at the point of maximum swelling is faster than in the case of swelling in benzene, and continues until $Q = 0.12$ gram-mole of chloroform in 100 grams of mixture. Starting from $Q = 0.13$ gram-mole in 100 grams of mixture, the increase in the degree of swelling is accompanied by a new decrease in the time of relaxation.

The character of the change in the time of relaxation of the vulcanizate on swelling may be explained if the heterogeneous structure of the intermolecular bonds of vulcanized rubber is taken into consideration. Let us assume that in the vulcanizate, together with chemical bonds between the chains, intermolecular forces (principally dispersion forces) between hydrocarbon units of the chains, and also the forces located in the polar oxygen-bearing and sulfur-bearing groups, play an essential role. The bonds governing the intermolecular activ-

ity differ in intensity and, consequently, the action of the solvent on these bonds differs. In the initial stage of swelling of vulcanized natural rubber, the flexibility of the bonds increases, since mixing with a low-molecular component increases the configurations. This is a consequence of the variable entropy of the mixture of the rubber with the solvent molecule. Since on deformation of the polymer, the change in the configurations of the chains proceeds according to the diffusion mechanism, the relaxation of stress proceeds more rapidly if there are more accessible configurations. Consequently in the initial stage of swelling, a decrease of the maximum time of relaxation τ^* is observed. However, swelling is accompanied by a simultaneous three-dimensional deformation of the network structure of the vulcanizate, and this causes a gradual straightening of the chain segments between the bonds. This straightening of the chains causes a decrease in the configurations, and at a definite stage of swelling (with preservation of the number of bonds), the time of relaxation of the vulcanizate increases. The ascending portion of the curve in Figure 6 corresponds to this stage. Maximum swelling is accompanied by an increase of the strain on the chain segments between the bonds of the network. As a consequence, the local intermolecular bonds (for example, the orientation or hydrogen bonds

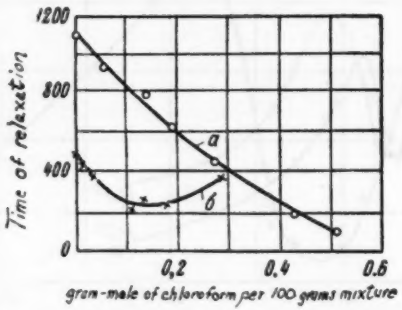

FIG. 8.—Relation of maximum time of relaxation of vulcanized polychloroprene at 10° C to swelling. (*a*) In chloroform. (*b*) In benzene.

between the oxygen-bearing and sulfur-bearing groups) begin to be destroyed. Destruction of these bonds increases the activity of the chains, and the time of relaxation decreases until the only chemical bonds remaining in the system are those which are stable at the prevailing temperature. Equilibrium in the system, it is understood, may be established before destruction of all the intermolecular bonds, since it is determined by the value of ΔS and ΔN. The second descending section of the curves in Figures 6 and 7 corresponds to this stage of the process.

This explanation agrees well with the influence of the temperature. As can be seen in Figure 7, an increase of the temperature from 15° to 30° C, without changing the character of the observed relationship, lowers the swelling curves, so that these curves become more nearly level. This is perfectly natural, since the increase in the temperature decreases the effect of the observed intermolecular energy.

The behavior of polychloroprene rubber is characteristic. If with swelling in benzene, the curve of the change of the time of relaxation passes through a minimum (Figures 6 and 8), then in chloroform (A in Figure 8) a steady decrease of the time of relaxation is observed. Undoubtedly this property of poly-

chloroprene rubber is the result of more intensive intermolecular activity than that of natural (isoprene) rubber, and of localization of this activity in the atoms of chlorine. Consequently the swelling of polychloroprene rubber in a nonpolar solvent (benzene) causes, first, destruction of the bonds between the carbon groups of the chains and, then, to a lesser extent, destruction of the bonds between the chlorine-bearing groups. With swelling in a polar solvent (chloroform), the local bonds between the chlorine-bearing groups are destroyed, and this causes a gradual increase of the activity of the chains and a decrease of the time of relaxation.

It should be noted that this explanation does not overlook the effect of entropy and the phenomena investigated. Furthermore, the decrease of the time of relaxation in the initial stages of swelling is connected with increased entropy of the mixture of high polymers with low polymers. However, from this point of view alone, it is impossible to explain the entire picture afforded by these experiments. A detailed explanation of all the phenomena requires a recognition of the varying intermolecular reaction in the vulcanizate and the possible destruction of the local intermolecular bonds as a result of the stress of the chain atoms between the bonds of the spatial network of the vulcanizate.

EFFECT OF SWELLING ON STABILITY OF VULCANIZED RUBBER

The change observed in the kinetics of high elastic deformation on swelling is noticeable in the process of multiple deformation of the swollen specimens.

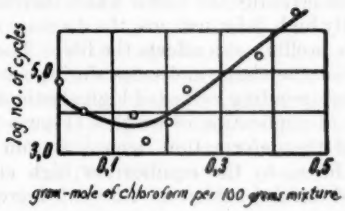

FIG. 9.—Relation of stability of vulcanized natural rubber to degree of swelling in chloroform; $t = 24.5°$ C.

An investigation of this effect was made in an apparatus quite similar to that shown in Figure 1. The difference between this and the apparatus described before was that the glass cylinder was oscillated by an electric motor by means of a system of levers. In addition, the apparatus was provided with a device to catch the carriage of weights after rupture of the specimen. The apparatus made possible changes in the frequency and ampltide of the oscillation of the cylinder and, consequently, also the frequency and amplitude of the deformation of the specimen of vulcanizate attached to the carriage.

In these experiments the frequency of oscillation was 85 cycles per minute, and the amplitude of deformation for all the specimens was 150 per cent of the original undeformed length.

The carriage with weights in the process of three-dimensional deformation draws further and further away from the upper clamp in proportion to the elongation of the specimen.

The results of these experiments are shown in Figure 9, where the life is expressed on the ordinate axis as the number of cycles of deformation which the test-specimen withstands before rupture. From these data it is evident that

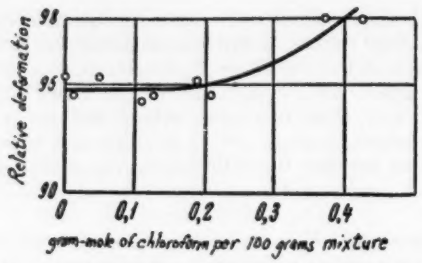

FIG. 10.—Relation of deformation of vulcanized natural rubber under periodic stress to degree of swelling in chloroform.

at low degrees of deformation (up to $Q = 1.13$ gram-mole of chloroform in 100 grams of vulcanizate) when the time of relaxation τ^* tends to increase, some decrease in life is observed. At deformation where the time of relaxation decreases, a notable increase in durability is observed. This relation between the time of relaxation and the life of the specimens is easily explained, since during increased activity of the chain molecules, if all other conditions are constant, high elastic deformation is accompanied by a decrease in the energy consumed in stretching the specimen. A part of this energy is consumed in overcoming internal friction and in activating the chemical processes which destroy the specimen. Hence, a decrease of the time of relaxation (an increase of the activity of the chains) is naturally the factor which increases the life of the vulcanizate. At sufficiently high deformations, the decrease of the tensile strength of the specimens due to swelling also affects the life. The above description of the change in activity of the chain molecules during swelling was proved experimentally by the corresponding values of high elastic deformation, observed at the given frequency of application of weights (Figure 10). Figure 10 gives data on the relation of the deformation, recorded from the application of a periodically changing force, to the equilibrium high elastic deformation of specimens of vulcanized natural rubber at different degrees of swelling.

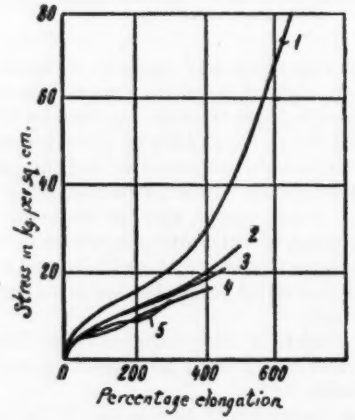

FIG. 11.—Stress-elongation of vulcanized polychloroprene at different degrees of swelling in benzene; 1-0; 2-6; 3-14; 4-16; 5-27 per cent.

The curves for vulcanized natural rubber and polychloroprene swollen in benzene or chloroform resemble each other. Figure 11 shows the corresponding curves for vulcanized polychloroprene swollen in benzene. It is evident that the curves become proportionately lower, the greater the degree of swelling of the specimen.

In all the cases studied, a sharp decrease of life was observed with increase in the degree of swelling. As distinguished from previously published data[6], a noteworthy decrease of the relative elongation with swelling was observed. The decreases of life and of relative elongation are especially sharp in the first stages of swelling. This can be explained as the result of conditions created in swelling which obstruct the crystalline phase during deformation. On the other hand, it should be remembered that, as a result of the unbalanced distribution of bonds in the spatial network formed by the heavier chemical valences, the chain molecules are successively broken during deformation. The less the disrupted molecules participate in the distribution of stress at highest deformation, the less does the intermolecular activity become. Thus the strong influence of swelling on the life and relative elongation of the vulcanizates can be explained.

CONCLUSIONS

1. The construction of an apparatus (elastometer) for the mechanical investigation of high elastic substances is described. This apparatus makes it possible to draw deformation curves and curves of the relaxation of stress at constant temperature and in different gaseous media, and also to investigate the life at multiple deformations. The sensitivity of the apparatus is: $\Delta P = 0.01$ g., $\Delta l = 0.01$ cm.

2. The molecular weight of the segments of the chains between the bonds of the spatial network of the vulcanizate, calculated by means of Flory's equation, increases with swelling, and approaches a certain maximum value. This is evidence of the rupture of the local intermolecular bonds on swelling.

3. The maximum time of relaxation, calculated according to the equation of Dogadkin, Bartenev, and Reznikovskiĭ[1], as a consequence of swelling, generally does not change uniformly; it decreases with swelling of natural rubbers in benzene and chloroform in the initial stages, then increases, and finally decreases again in the last stages of swelling.

4. An increase of temperature displaces the minimum times of relaxation to lower degrees of swelling.

5. The increase of the maximum time of relaxation as a result of swelling causes a decrease of the life of the vulcanizate; a decrease of this factor is accompanied, at least within certain limits, by an increase of life.

6. Swelling causes a decrease of tensile strength and of the relative elongation of vulcanizates.

7. The changes recorded above in the equilibrium and kinetic characteristics of high elastic deformation are explained by the presence in the vulcanizate of different intermolecular bonds.

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COMMENT ON "RELATIONSHIP BETWEEN GOUGH-JOULE COEFFICIENTS AND MODULI OF VULCANIZED RUBBERS" *

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In an article of the title quoted above Conant, Hall, and Thurman[1] were interested in establishing by experiment the theoretical equality between the tangent shearing modulus of a rubber and the ratio of the temperature coefficient of shearing stress to the negative temperature coefficient of shearing strain. Their published data can be used also for calculating the value of an important property, the relative temperature coefficient of relative stress, σ, at constant strain, γ, or $T/\sigma(\partial\sigma/\partial T)_\gamma$. The value of this coefficient is unity if there is entropy change but no energy change in an isothermal strain, as is postulated in the kinetic theory of elasticity.

The values of the coefficient can be calculated from the data given by Conant, Hall, and Thurman for σ/γ, $1/\gamma(\partial\sigma/\partial T)_\gamma$, and T, the reference temperature.

The calculations yield the results:

Compound	$T/\sigma(\partial\sigma/\partial T)_\gamma$
Hevea B	0.82
GR-S	1.33
Butaprene	0.90
Butyl	1.05
Neoprene	1.04
Hevea A	0.81
Hevea C	0.67

Although the values of the coefficient are correct in order of magnitude, they depart from unity in many cases by amounts which are presumably larger than the experimental error. These results are qualitatively in agreement with those published by Copeland and Mooney[2], who also found significant departures from the theoretical value, unity, in several cases. Quantitatively, however, the results of the two groups of experimentalists are not in good agreement.

Obviously more work in the field of thermo-elasticity is called for to determine whether the differences in results are caused by the use of different compounds, different test methods, or other factors. However, it is growing more and more evident that, contrary to the kinetic theory of elasticity, the energy of an elastomer subjected to isothermal strain sometimes contributes appreciably to the stress.

Concerning the experimental method used by Conant and associates, it may be remarked, incidentally, that the constraints on the thermal expansion imposed by a sandwich type of sample involves some corrections which may be appreciable, and certainly are not easily estimated.

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* Reprinted from the *Journal of Applied Physics*, Vol. 21, No. 12, page 1338, December 1950.

APPLICATION OF X-RAY DIFFRACTION METHODS TO THE IDENTIFICATION OF NATURAL AND SYNTHETIC RUBBERS

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SCOPE

This paper discusses the development of applications of x-ray diffraction methods to the identification and study of natural and synthetic rubber stock types as part of a broad elastomer research program. The investigations conducted to date include applications of (1) film techniques for the qualitative identification of representative rubber types and rubber compounding ingredients, and for the quantitative estimation of crude and reclaimed rubber mixtures, and (2) Geiger counter spectrometer techniques for the qualitative identification of representative rubber types.

IDENTIFICATION OF COMPOUNDING INGREDIENTS BY FILM TECHNIQUES

x-Ray diffraction methods have been used in various studies of compounding ingredients[1].

A comparison of a list of the various compounding ingredients for the several stocks furnished for this investigation with the A.S.T.M. Index of Diffraction Patterns[2] showed that data on only a few of the compounding ingredients have been catalogued. It was, therefore, necessary to prepare and index patterns, where such were unavailable, for all the compounding ingredients in the uncombined form.

The powder method of x-ray diffraction analysis was used in these studies. Identification data, including relative line intensity values determined from densitometer measurements, are included in Table 1. The patterns of the rubber stocks, prepared for the determination of the compounding ingredients, were obtained by centering a small strip of rubber in a powder camera.

Visual comparison of the rubber stocks and compound ingredient patterns was used to determine which of the compounding ingredients could be detected in the rubber stocks. The results show that major solid compounding ingredients which remain in uncombined form after vulcanization of the elastomers can be readily identified by this method. Such factors as crystallinity, absorptivity, amount present, and retention of form affect the ease of identification of compounding ingredients in rubber stocks. The method has the advantage over chemical methods in that it yields information about the crystalline or molecular form in which an ingredient is present. It may be interesting to note that a comparison of six commercial compounding ingredients, viz., Pelletex, Micronex, P-33, Philblack-A, Statex-B, and Thermax, indicated that

* Condensed from a paper published in the *ASTM Bulletin*, No. 171, pages 71–80, January 1951.

TABLE I

X-RAY DIFFRACTION DATA FOR COMPOUNDING INGREDIENTS

Material	d	I/I_0	Material	d	I/I_0
Altax	13.5	1.00	Neozone-A	4.40	1.00
	5.45	0.73		4.51	0.96
	3.56	0.72		3.60	0.96
	3.99	0.41		11.40	0.83
	3.08	0.33		3.50	0.67
Captax	7.60	1.00	Polyac	3.54	1.00
	3.13	0.87		7.12	0.97
	3.76	0.78		5.63	0.83
	3.19	0.67		4.43	0.66
	3.84	0.49		2.34	0.55
Heliozone	4.13	1.00	Stearic acid	4.13	1.00
	3.72	0.71		3.75	0.10
	2.48	0.13		3.99	0.05
	4.58	0.09		4.35	0.04
	2.22	0.09		13.2	0.03
Diphenylguanidine	4.63	1.00	Tuads	3.42	1.00
	10.3	0.58		5.62	0.94
	4.14	0.32		4.95	0.37
	3.47	0.31		4.73	0.36
	4.46	0.28		6.27	0.21
Litharge	See A.S.T.M. Data Card No. 1999(3) or 1981(4)		Thionex	5.85	1.00
				3.58	0.72
Magnesia	See A.S.T.M. Data Card No. 3286(3) or 3424(4)			6.54	0.49
				3.45	0.49
Sulfur	See A.S.T.M. Data Card No. 1131(3) or 1082(4)			4.69	0.48
Vandex	See A.S.T.M. Data Card No. 2070(3) or 2118(4)				
Zinc Oxide	See A.S.T.M. Data Card No. 2911(3) or 3079(4)				

they are nearly similar, and are low crystallinity carbon, although closer study[3] has shown that no two carbon blacks give the same x-ray pattern.

IDENTIFICATION OF RUBBER TYPES BY FILM TECHNIQUES

ROOM TEMPERATURE STUDIES

The fundamental criterion used in the appraisal of x-ray diffraction methods for the identification of natural and synthetic rubbers is whether they can be made to yield distinctive patterns. Natural and synthetic rubbers are commonly classed as amorphous, as opposed to crystalline substances. Thus an x-ray pattern of unstretched rubber is characterized by blurred rings or halos at low Bragg angles. Under these conditions patterns for different types are not readily distinguishable. However, it has been shown in recent years that, under suitable conditions of stretching, temperature, and pressure, some of these materials show properties associated with crystallinity, while others do not. Katz[4] first applied x-ray diffraction methods to the study of stretched natural rubber, and showed that it gives a fiber pattern with sharp interference spots. The position of these spots are independent of the degree of stretching, but their intensities increase proportionally to it. Mark and Whitby[5] have reported that crystallization can be induced in some types of rubber by subjecting

them to specific low temperature treatments. Hansen and Halverson[6] and Beu, Reynolds, Freyling, and McMurry[7] have reported evidences of crystallinity in some rubber materials on reduction of temperature and stretching.

Even in cases where no crystallinity was observed, a high degree of stress was found to produce intensification of the amorphous halos[8]. It should be noted that the crystallinity results referred to above were obtained by different methods, including thermal, optical, mechanical, specific volume, and x-ray diffraction measurements.

In view of the above findings, it was decided to investigate the diffraction patterns of representative rubber stocks under various combinations of stretching and (or) aging with a view of determining the best conditions for clear identification.

Since elastomers produce x-ray reflections at low Bragg angles, all patterns were recorded on flat films, using transmission techniques.

A study of the several rubber stock patterns carried out in the stretched condition at room temperature shows that distinctive fiber patterns are obtained for Hevea, GR-M, and GR-I, whereas little change in the diffuse halos is noted for GR-S, nitrile rubber, and Thiokol.

LOW-TEMPERATURE FILM STUDIES

To study the elastomers at low temperatures, a special sample holder, with provision for cooling, was designed and constructed. Photographs of the cooling unit, experimental set-up, and sample holder are shown in Figures 1, 2, and 3.

Transmission patterns were made on each of the stocks in the special low-temperature camera. Thin strips of the rubber samples were exposed in the unstretched state, both at room temperature (with no aging), and frozen at $-70°$ F after being aged in a constant-temperature box. The aged samples were frozen on dry ice and then transferred to the camera in the sample holder,

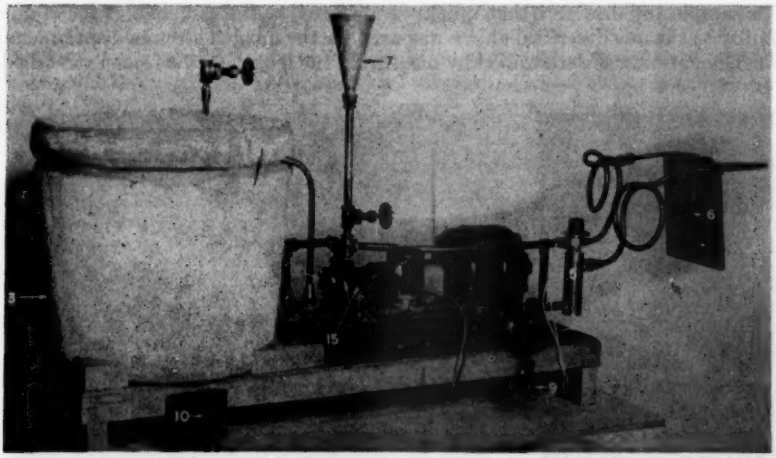

FIG. 1.—Photograph of Cooling System (before lagging). 1.—Motor; 2.—pump; 3.—low-temperature bath; 4.—solenoid valve; 5.—thermostat; 6.—sample holder block; 7.—filling funnel; 8.—vent; 9 and 10.—drain valves; 15.—needle valve.

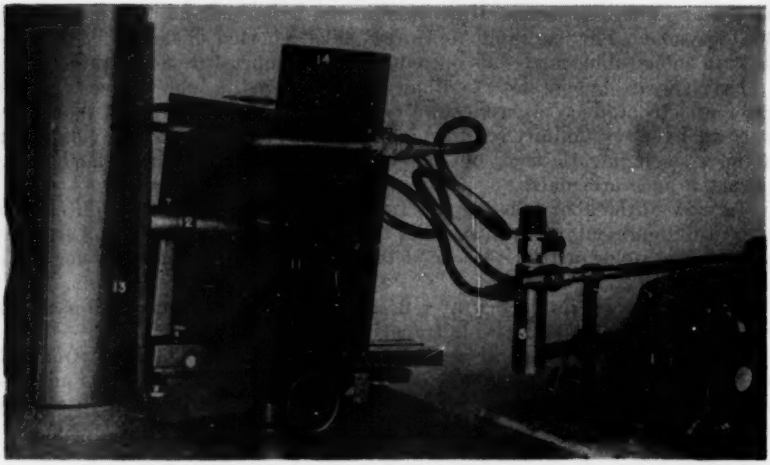

FIG. 2.—Camera for low temperature x-ray diffraction. 1.—motor; 5.—thermostat; 11.—bakelite box; 12.—collimating tube; 13.—x-ray tube housing; 14.—film cassette.

which was precooled on dry ice. This prevented the sample from warming during transfer to the camera.

To obtain patterns for the aged stretched samples, the following procedure was used. The aged samples were immersed in an alcohol-dry ice bath at −30° F, which is low enough to prevent melting of the rubber crystals, yet high enough to make possible elongation of the samples. After stretching the samples in the bath, the temperature was reduced to −70° F to freeze the samples in the stretched condition. The stretched frozen sample was placed in the groove of the sample holder disc, which was imbedded in a block of dry ice. The sample and disc were then quickly transferred to the camera. A technique similar to the one described above was used for the unaged stretched specimens. The elongation was determined by measuring the length of the frozen stretched

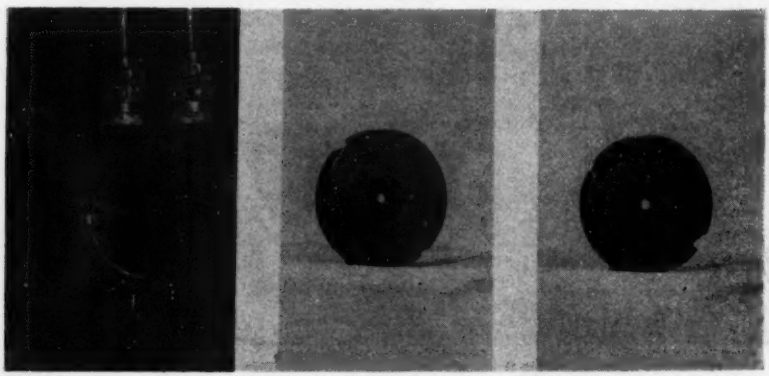

FIG. 3.—Sample holder for low temperature x-ray diffraction.

TABLE II

TYPE PATTERNS OBTAINED UNDER DIFFERENT EXPOSURE CONDITIONS FOR RUBBER STOCKS

Conditions of exposure	Hevea	GR-S	Perbunan-26	GR-M	Thiokol-FA	GR-I
Room temperature, unstretched	Diffuse rings	Diffuse rings	Diffuse rings	Diffuse rings	Diffuse rings	Diffuse rings
Room temperature stretched	Fiber pattern 400% elong.	Diffuse rings 400% elong.	Diffuse rings 400% elong.	Fiber pattern 400% elong.	Diffuse rings 350% elong.	Fiber pattern 300% elong.
Stretched at room temperature, frozen at −70° F	Fiber pattern 400% elong.	Diffuse rings 400% elong.	Diffuse rings 400% elong.	Fiber pattern 400% elong.	Fiber pattern 350% elong.	Fiber pattern 300% elong.
No aging stretched at −30° F frozen at −70° F	Fiber pattern 350% elong.	Diffuse rings 400% elong.	Diffuse rings 250% elong.	Fiber pattern 360% elong.	Diffuse rings 340% elong.	Fiber pattern 300% elong.
Aged at −25° F for 64 hours, unstretched, frozen at −70° F	Sharp rings	Diffuse rings	Diffuse rings	Diffuse rings	Diffuse rings	Diffuse rings
Aged at −25° F for 64 hours, stretched, frozen at −70° F	Sharp rings and intense spots 225% elong.	Diffuse rings 230% elong.	Diffuse rings 240% elong.	Fiber pattern 370% elong.	Fiber pattern 200% elong.	Fiber pattern 260% elong.

sample, and comparing it with the length of the relaxed sample, measured after removal from the camera.

Patterns were taken on all samples under the following conditions:

(1) Room temperature, unstretched.
(2) Stretched at room temperature and frozen.
(3) Unaged, stretched at −30° F, frozen.
(4) Aged at −25° F for 64 hours, unstretched.
(5) Aged at −25° F for 64 hours, stretched.

A summary of all results is contained in Table II. Samples of typical patterns of Hevea are shown in Figure 4. Examination of Table II shows that Hevea, GR-M, Thiokol-FA and GR-I can be made to produce characteristic

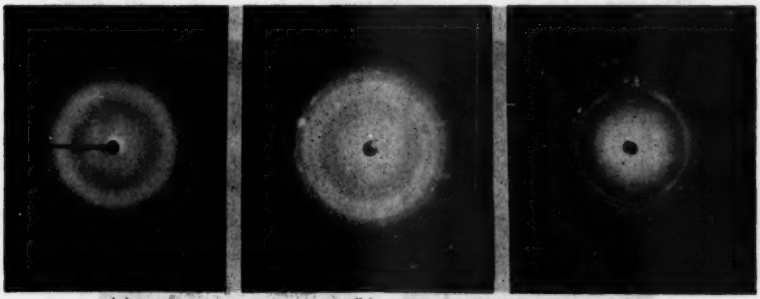

FIG. 4.—*x*-Ray diffraction patterns for Hevea under various treatments. (a) room temperature, unaged; (b) aged, unstretched; (c) aged, stretched.

crystalline patterns under one or more conditions reported, whereas GR-S and nitrile rubbers show diffuse rings under all conditions of test.

QUANTITATIVE ESTIMATION OF RUBBER MIXTURES BY FILM TECHNIQUES

To determine whether film techniques could be used for the estimation of rubber mixtures, samples of known content of crude and reclaimed stocks were run in the stretched condition at room temperature. The results of this test are shown in Figure 5. A plot of density of A-1 spots against the percentage of crude rubber, Figure 6, indicates the possibility of using x-ray diffraction methods for the semiquantitative estimation of an ingredient which crystallizes on stretching.

It must be noted, however, that such a graph can be applied only to mixtures prepared in an identical manner. The use of varying grades of reclaimed stocks may result in errors of measurement in view of the variable density of the fiber-pattern spots. The reclaiming process appears to destroy the crystallite formation of Hevea rubber on stretching, by virtue of a breakdown in molecular size during mastication. The severity of the mastication process and the grade of reclaimed stock employed determine the extent of this breakdown. Hence, in some cases a reclaimed stock may exhibit crystallite formation when stretched, with a consequent recording of a fiber pattern on x-ray diffraction analysis. However, use of a graph such as this gives a measure of the relative amount of crystallized rubber in the mixture; hence if the reclaimed

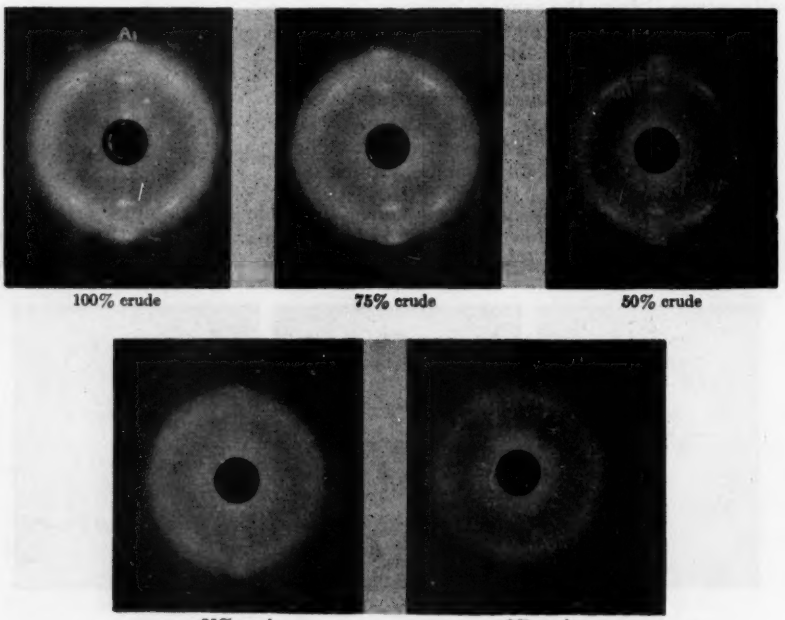

FIG. 5.—x-Ray patterns for mixtures of crude and reclaimed rubber.

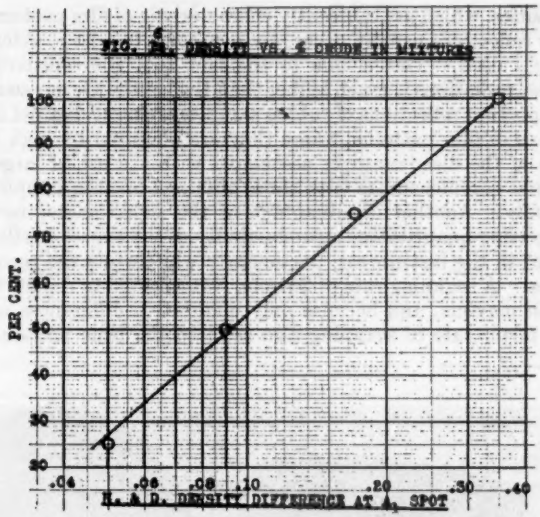

FIG. 6.—Density vs. % crude in mixtures.

rubber is of a grade which can be crystallized by stretching, the build-up of the pattern signifies that the quantity of crude rubber present is greater. It must be understood that for measurements such as this, all experimental conditions should be standardized, including thickness of sample, exposure conditions, and especially the percentage elongation. This latter factor is of particular importance, because, although the positions of the diffraction spots are characteristic of the elastomer, the intensity of the spots depend on the quantity of crystallites present, and this is determined (among other things) by the percentage elongation of the sample.

GEIGER COUNTER SPECTROMETER TECHNIQUES FOR THE QUALITATIVE IDENTIFICATION OF RUBBER TYPES

The use of an x-ray spectrometer[9] suggested several advantages over film methods. To begin with, since the diffraction effects produced by these rubbers occur below 20° C (Bragg angle), the time necessary to run a spectrometer trace is of the order of twenty minutes at 2 r.p.m. scanning speed, compared with an average of two hours for film exposures. The need for film processing and sensitometry is eliminated, as well as the problem of determining specimen to film distance. The spectrometer traces can be interpreted more easily, since both reflection angles and intensities can be taken directly from the trace. The use of larger specimens makes for better sampling and minimizes the danger of breakage of the sample.

The reflection technique utilized in the spectrometer reduces the difficulties of controlling the thickness of specimen, which is more important in film techniques when transmission is used. The variations in intensity arising from differences in the thickness of the sample in film techniques are far greater than the variations in intensity resulting from penetration and absorption effects of the incident radiation in the spectrometer. The difficulties due to high back-

ground intensities, which are inherently characteristic of film patterns in regions where rubber reflections usually occur, are overcome to a large extent when the spectrometer is used. This is due to the fact that the sensitivity of silver halides to these radiations is much higher than that of the Geiger counter. As a result, the important reflections of rubber samples are more distinct in spectrometer traces than in film patterns, where they are obscured by high background effects. One of the disadvantages associated with the use of large samples is that elongations commensurate with those obtained on thin samples cannot be obtained readily. Another disadvantage of the spectrometer method is the difficulty of getting quantitative reproducibility of the traces, partly because of errors inherent in the instrument, particularly when using the recorder at fast scanning rates. A scanning rate of 2 r.p.m. was selected to reduce the width of the diffraction maxima, and because only qualitative differences were investigated. The faster rate of scanning also reduced the time necessary to run a pattern.

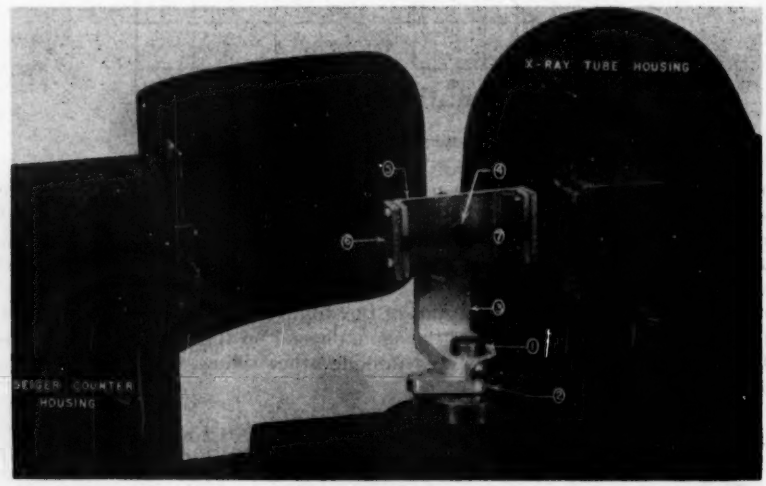

FIG. 7.—Test set-up for x-ray spectrometer rubber identification. 1.—shaft; 2.—positioning collar; 3.—L-shaped bracket; 4.—shaft; 5.—channel; 6.—clamp; 7.—rubber specimen.

Samples about $\frac{1}{2}$ inch wide and $\frac{1}{16}$ inch thick were placed in a stretched condition in a conventional spectrometer by means of a special sample holder (Figure 7). The specimen was set with the direction of stretching horizontal, as this position yielded the highest intensities, and was aligned so that it was tangent to the focussing circle of the instrument.

Traces were run at a scanning rate of 2 r.p.m. for the 2θ range of 4 to 38°, which includes the important diffraction lines of the samples being studied. All traces were made with the same amplitude and damping settings, except for GR-I, in which case it was necessary to decrease the amplitude setting. Figure 8 shows the traces for the standard stocks of the six rubber types in the stretched condition, with angles expressed in degrees 2θ. Table III shows a comparison of the characteristic reflections of the rubbers (the reflections of the compounding ingredients are not included). The d values were measured at

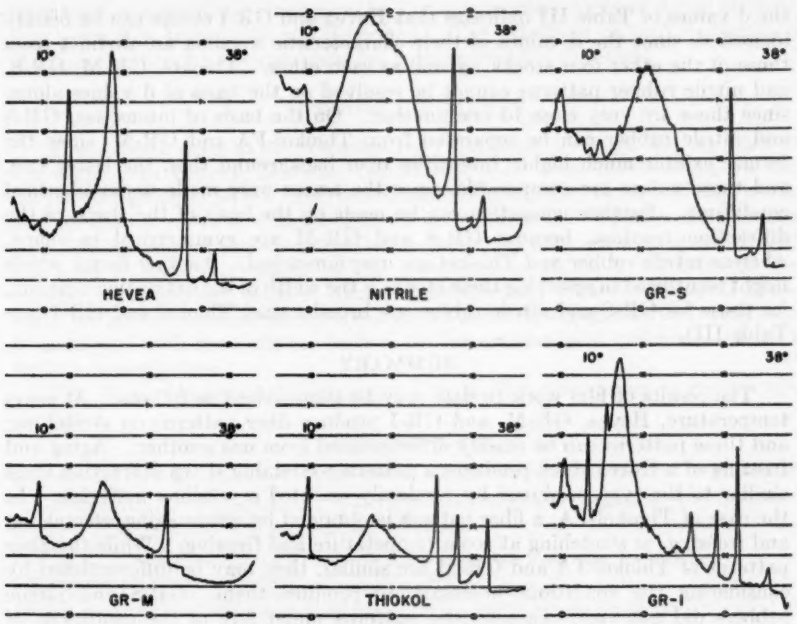

FIG. 8.—*x*-Ray spectrometer patterns for six representative types of rubber.

the points where the maxima occurred. Since most of the stocks contained zinc oxide, its reflections were used as an internal standard to overcome errors arising from slippage and nonuniformity of the recorder chart paper.

The patterns for all stocks in the stretched condition, except nitrile, rubber and GS-S, showed an improvement in intensity and sharpness of the diffraction maxima over those obtained in the unstretched state, as was evident from the film work. In the case of Hevea, the single diffuse ring gave two sharp reflections in the stretched sample which correspond to the intense spots at 12 or 6 o'clock shown in the film pattern. Consideration of traces (Figure 8), and

TABLE III

X-RAY SPECTROMETER DATA FOR REPRESENTATIVE RUBBER STOCKS

Rubber stock	% Elongation	D values for characteristic maxima (A°)	Width of reflection (degrees 2θ)	Intensity over background	Shape of reflection
Hevea rubber	430	4.27	8.0	6.0	Symmetrical
		6.22	2.0	4.39	Symmetrical
GR-M	300	4.57	11.2	2.20	Symmetrical
Perbunan 26	330	4.69	16.2	4.99	Unsymmetrical
Thiokol-FA	100	4.57	12.4	1.72	Unsymmetrical
GR-S	220	4.48	16.4	4.27	Symmetrical
GR-I	350	5.99	10.4	5.71	Symmetrical

the d values of Table III indicates that Hevea and GR-I stocks can be readily identified, since the d values of their characteristic maxima are distinct from those of the other four stocks, as well as each other. Thiokol, GR-M, GR-S, and nitrile rubber patterns cannot be resolved on the basis of d values alone, since these are very close to one another. On the basis of intensities, GR-S and nitrile rubber can be separated from Thiokol-FA and GR-M, since the former exhibit much higher intensities over background than the latter two, and these values are comparable, since the traces were made under identical conditions. Further separation can be made on the basis of the shape of the diffraction maxima, because GR-S and GR-M are symmetrical in shape, whereas nitrile rubber and Thiokol are unsymmetrical. Another factor which might be utilized in resolving these stocks is the width of the diffraction maxima, for those for GR-S and nitrile rubber are broader than Thiokol and GR-I (see Table III).

SUMMARY

The results of film work to date may be summarized as follows. At room temperature, Hevea, GR-M, and GR-I produce fiber patterns on stretching, and these patterns can be readily differentiated from one another. Aging and freezing of a Hevea stock produces a pattern containing sharp diffraction rings similar to the type produced by randomly oriented crystalline materials. In the case of Thiokol-FA, a fiber pattern is obtained by either aging, stretching, and freezing, or stretching at room temperature and freezing. While the fiber patterns of Thiokol-FA and GR-M are similar, they may be differentiated by considering the conditions necessary to produce them. GR-S and nitrile rubbers did not yield characteristic patterns under any of the conditions of treatment.

The results obtained on the x-ray spectrometer indicate that the six stocks considered in these tests can be made to yield distinctive patterns when examined in the stretched condition. This is accomplished through consideration of the location, intensity, breadth, and shape of the characteristic reflections of the different stocks. Traces run on the six cold-resistant stocks showed the characteristic rubber reflections to be similar to the standard types.

FUTURE WORK

In the immediate future, methods for extending the use of the x-ray spectrometer to the identification of compounding ingredients will be developed. This work appears to be justified, since potential economies over film techniques in time and money are indicated.

Further problems which could be investigated by x-ray diffraction methods include: (1) quantitative determination of mixtures of the several types of rubber, with a view to setting up working curves to be utilized in the analysis of unknown mixtures (2) the establishment of combined x-ray diffraction and optical emission spectroscopy techniques for the quantitative analysis of compounding ingredients, and (3) determination of crystallinity induced as a function of elongation and relaxation under various conditions for representative rubber stocks and mixtures.

SUMMARY

In this paper, x-ray diffraction patterns and data for rubber compounding ingredients are presented and applied to the identification of major crystalline ingredients in several basic rubber stock types. Methods for the identification

of natural and synthetic elastomers by low temperature aging and (or) stretching, using film techniques, are described. The extension of such methods to the Geiger counter x-ray spectrometer is presented and discussed.

ACKNOWLEDGMENTS

The authors wish to acknowledge their gratitude to N. A. Kahn, head of the Metallurgy Branch, Material Laboratory, New York Naval Shipyard, for his encouragement, advice, and consultation during the conduct of the work, and for his review of the manuscript on its completion. Thanks are also due to J. Bland, now of the Welding Development Section, for his supervision of the work in the initial stages of the investigation, to C. K. Chatten of the Rubber Development Section, Material Laboratory, New York Naval Shipyard, for his cooperation during the conduct of the work, and to C. Davis, who is associated with the authors' section, for his assistance in gathering the data for this investigation.

The Navy Department's permission to publish this paper is greatly appreciated.

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CRYSTALLIZATION AND SECOND-ORDER TRANSITIONS IN SILICONE RUBBERS *

C. E. Weir, W. H. Leser, and L. A. Wood

INTRODUCTION

Most of the properties of silicone rubbers (polysiloxanes), developed especially for use at high temperatures, have been found to show less change with temperature than those of other polymers[1]. Recently there has been particular interest in the properties of all types of rubbers at low temperatures. Consequently the behavior of silicone rubbers at low temperatures has taken on additional importance.

The fundamental phenomena related to the stiffening of rubbers at low temperatures are the second-order transition[2] and crystallization[3]. Both of these phenomena influence the relationship between the dimensions of a specimen and the temperature. In the present investigation the change of length at different temperatures was measured with an interferometer.

MATERIALS INVESTIGATED

The samples of silicone rubber were of commercial origin. Two of them contained no fillers or vulcanizing agents and were highly elastic brown solids of low strength. They transmitted light relatively well, and had refractive indices of 1.4028 and 1.4040, respectively. The densities, measured by the method of hydrostatic weighing, were found to be 0.973 and 0.974 g. per cc. at 25° C, respectively. These densities appear to be slightly higher than densities of liquid silicones previously reported[4]. These samples were produced by the General Electric Co. and were supplied through the kind coöperation of the Connecticut Hard Rubber Co. They are designated General Electric 9979G silicone rubber and in this paper are referred to as gum silicones for convenience.

The other samples of silicone rubber contained filler and were vulcanized. These were obtained through the coöperation of the Dow-Corning Co. and were designated Silastic X-6073 and Silastic X-6160. These types were especially designed for use at low temperatures. Silastic X-6160 is described as differing only slightly from Silastic 160, which has been reported[5] to contain 60 per cent of filler consisting of equal weights of zinc oxide and titanium dioxide. No data are available on the other varieties of Silastic.

A vulcanizate of Silastic 250, a new variety of silicone rubber, was also furnished by the Dow-Corning Co.

EXPERIMENTAL METHOD

The interferometer arrangement described by Wood, Bekkedahl, and Peters[6] was used, with minor modifications, to determine the thickness of rubber specimens as a function of temperature. The apparatus was modified by surrounding the lower removable portion of the interferometer container with close-

* Reprinted from the *Journal of Research of the National Bureau of Standards*, Vol. 44, No. 4, pages 367–372, April 1950.

wound, close-fitting helix of ¼-inch copper tubing. The lower end of the helix was terminated in a wye, one leg of which terminated in a fine orifice. The other leg of the wye passed through the wall of the container and terminated in a somewhat larger orifice. Dry carbon-dioxide-free air was used to eliminate clogging of lines by freezing of vapors. This air flowed into the upper end of the helix at a pressure of 1 cm. of mercury, circulated through the coil, and was discharged into both the surrounding Dewar and the interferometer chamber. Internal and external stirring and a markedly lower temperature gradient resulted from the use of this air stream. After the air had passed through the interferometer chamber, it was discharged across the top glass plate of the container, thereby effectively eliminating condensation of moisture on this plate. Liquid nitrogen, used as a coolant, produced temperatures as low as −196° C. The cooling was effected in a manner similar to that described previously[6].

The light source consisted of a helium discharge tube. Essentially monochromatic light of wave-length 5876 Å was obtained by use of appropriate filters.

The top interferometer plate, a semicircular disk of fused quartz 2 cm. in diameter and 2 mm. thick, which was supported by the test-specimens, weighed 0.82 gram.

No correction for change in refractive index of air with temperature was applied to the data obtained.

Slabs of silicone rubber were accurately cut with parallel faces by means of a sharp blade and a small miter box. One to three specimens, generally 4-mm. cubes, cut from a slab were placed between the two interferometer plates, with the parallel faces of the specimens in contact with the plates. After removing the eyepiece of the telescope, the elastic specimens were moved about between the interferometer plates until the images of the slit reflected from the upper and lower plates appeared to coincide. Fringes of the desired width were clearly visible when the eyepiece of the telescope was replaced.

Measurements below temperatures at which rubbers crystallized presented two main difficulties; first, maintaining visible fringes during the dimensional changes occurring on freezing; and second, maintaining a uniform rate of cooling at low temperatures.

Attempts were made to obtain fringes with crystalline material by cooling the specimens by immersion in liquid nitrogen and then manipulating the frozen specimens with suitable prods so as to produce fringes. These attempts were unsuccessful principally because of frosting of all exposed surfaces, and therefore measurements were made below −100° C only in a few fortuitous experiments in which fringes were maintained during crystallization.

Measurements of expansion were found to be difficult to obtain on cooling at very low temperatures, since the height of the liquid nitrogen in the surrounding Dewar was necessarily such that intermittent contact occurred between the coolant and the exterior of the interferometer container. Such contact produced rapid and nonuniform cooling. A rate of cooling or heating of about 1 degree C per minute was considered desirable in these experiments[6]. Most measurements at low temperatures were made on heating and were carried out by cooling the interferometer to −196° C, insulating the system, and permitting it to warm by absorption of heat from the surroundings.

RESULTS AND DISCUSSION

Graphical results shown in the succeeding figures are typical, but do not include measurements on all specimens of silicone rubber investigated. In most instances only those portions of the curves are shown that are considered pertinent to the discussion.

Crystallization on cooling to low temperatures, manifested as a radical decrease in specimen length on cooling over a narrow temperature interval, was observed in all samples except Silastic X-6073. Melting, observed as the reverse process on heating, was found above the crystallization temperature in all samples except X-6073.

Expansion curves on cooling and heating a gum silicone are shown in Figure 1. Crystallization is believed to occur between $-60°$ and $-67°$ C. This temperature range of crystallization was found in the gum silicones and Silastic

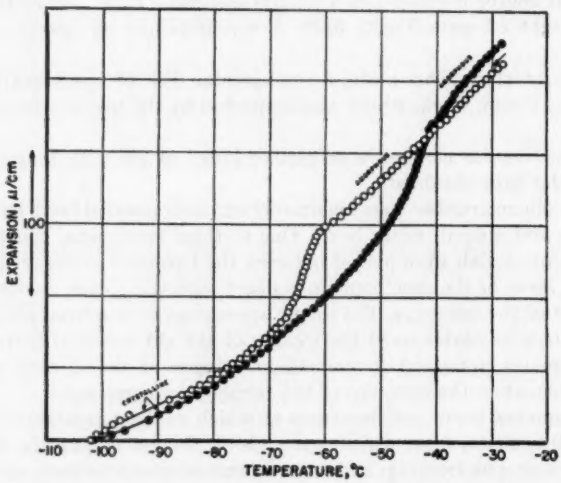

FIG. 1.—Crystallization and melting of gum silicone. Average thickness at 20° C, 0.414 cm. Values for expansion are calculated in terms of the thickness at 20° C. ○, Observations on cooling; ●, observations on heating.

X-6160 (Figure 5). Results obtained with Silastics X-6073 and 250 are somewhat different, and will be described in detail later. The crystallization depicted by Figure 1 appears to be a rapid process, in contrast to the crystallization of natural rubber studied by Bekkedahl and Wood[7]. Attempts to vary the temperature at which crystallization occurred or to produce supercooled material by rapidly chilling the interferometer in a liquid nitrogen bath were not successful, as specimens invariably crystallized near $-60°$ C. The values for hardness of several varieties of Silastic at temperatures as low as $-62°$ C are reported by Konkle, Selfridge, and Servais[6]. All the values show a rapid rise at the lowest temperature measured. They found that the equilibrium hardness values at temperatures below $-55°$ C were not attained until after 3.5 hrs. Both of these observations are indicative of the crystallization reported in the present paper.

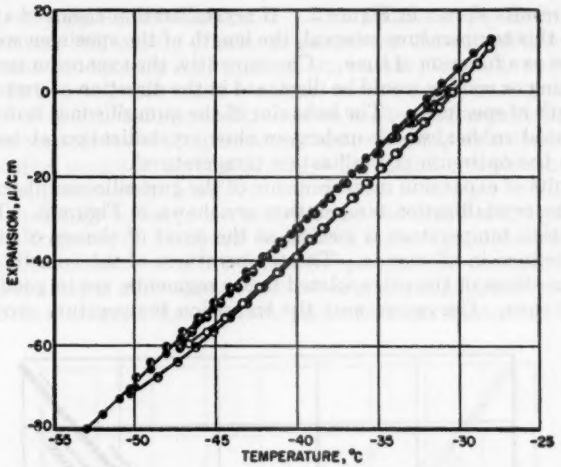

FIG. 2.—Behavior of gum silicone above the crystallization temperature. Average thickness of 20° C, 0.414 cm. Values for expansion are calculated in terms of the thickness at 20° C. ◐, Observations on first cooling; ◓, observations on first heating; ◒, observations on second cooling; ○, observations on second heating; ●, observations on third cooling.

The onset of melting with increasing temperature is not sharp. It is believed that melting begins a few degrees above the crystallization temperature and is complete at about −39° C.

The magnitude of the volume change associated with crystallization of gum silicones appears to be variable and as calculated from linear changes ranges from 2.0 to 7.8 per cent. The maximum volume change on crystallization of natural rubber has been found to be slightly over 3 per cent.[3]

If specimens of gum silicone are alternately cooled and heated cyclically at temperatures somewhat above −60° C, no evidence of crystallization or melting is observed. Experiments of this nature, carried out between −30° and −50°

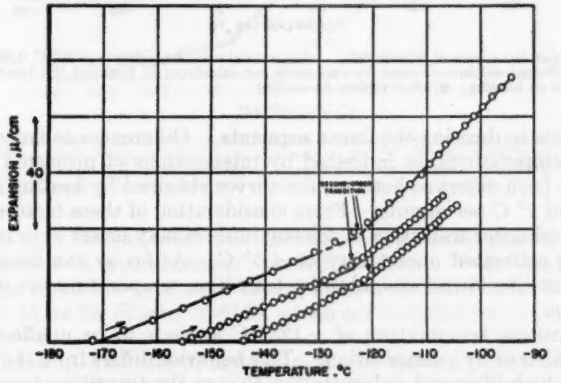

FIG. 3.—Second-order transitions of GE 9979G gum silicone. Average thickness at 20° C., 0.424 cm. Curves plotted from different origins. Values for expansion are calculated in terms of the thickness at 20° C.

C gave the results shown in Figure 2. If crystallization occurred at a measurable rate in this temperature interval, the length of the specimen would gradually decrease as a function of time. Consequently, the expansion curves on successive heating or cooling would be displaced in the direction corresponding to a smaller length of specimen. The behavior of the gum silicones is in contrast to that of natural rubber, which undergoes slow crystallization at temperatures higher than the optimum crystallization temperature[5].

The results of expansion measurements of the gum silicones at temperatures far below the crystallization temperature are shown in Figure 3. The second-order transition temperature is located as the point of change of slope, and is fairly well defined in all curves. The temperatures of the transitions, defined as the intersections of the extrapolated linear segments, are in good agreement on repeated runs. Curvature near the transition temperature produces obvi-

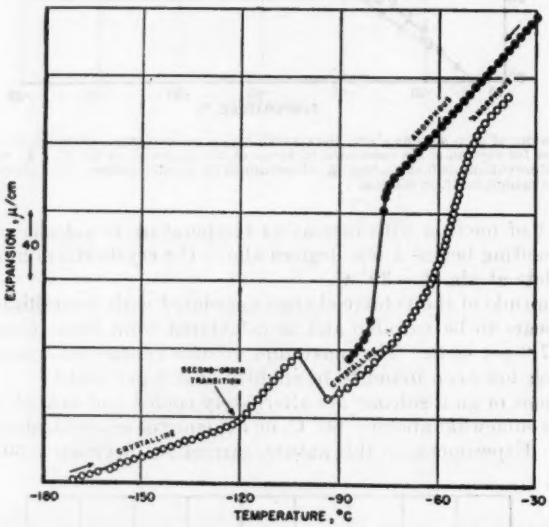

FIG. 4.—Expansion curves of Silastic 250. Average thickness of specimens at 20° C, 0.386 cm. Curves plotted from different origins. Values for expansion are calculated in terms of the thickness at 20° C. ○, Observations on heating; ●, observations on cooling.

ous difficulties in drawing the linear segments. Differences as large as 5° C in transition temperatures, as indicated by intersections of projected linear segments, have been observed between the curves obtained by heating and cooling at the rate of 1° C per minute. From consideration of these factors it appears the the second-order transition of silicone rubbers may be set at −123° C, with a maximum estimated uncertainty of ±5° C. As far as can be ascertained, this represents the lowest second-order transition temperature yet reported for any polymer.

The transition temperature of −123° C appears to be unaffected by the addition of filler or by vulcanization. This behavior differs from that of natural rubber[2] in which filler and vulcanization change the transition temperature.

Silastic 250 differed from the other silicones in its temperature of crystallization, which was appreciably lower, and in the fact that it could be super-

cooled, with only partial crystallization. The results of expansion measurements obtained on this variety of silicone rubber are shown in Figure 4.

Observations on heating and cooling shown in Figure 4 were obtained separately. It is noted that while a normal second-order transition temperature of −121° C is obtained, crystallization on cooling and completion of melting on heating occur at lower temperatures than previously described. Crystallization on cooling occurs at approximately −75° C and completion of melting on heating at approximately −45° C.

There is evidently a range of temperature favorable for crystallization which extends from −75° to about −100° C, since crystallization of supercooled material was observed at the latter temperature on increasing temperature. This behavior is very similar to that of natural rubber,[8] which can be crystallized over a range of temperatures and which can be supercooled.

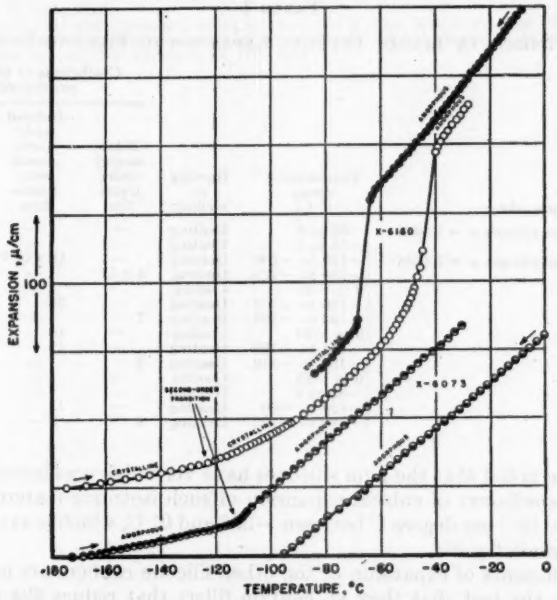

FIG. 5.—Expansion curves of Silastics X-6073 and X-6160. Curves plotted from different origins. Values for expansion are calculated in terms of the thickness at 20° C. Silastic X-6073: average thickness at 20° C, 0.326 cm; ◓, observations on heating; ◒, observations on cooling. Silastic X-6160; average thickness at 20° C, 0.385 cm; ○, observations on heating; ●, observations on cooling.

Silastic X-6073 differed from the other silicone rubbers in that it showed no evidence whatever of crystallization or melting between −180° and 0° C. A portion of the results of expansion measurements obtained with this variety, together with those for Silastic X-6160, which are included for comparison, are given in Figure 5.

X-6073 shows no evidence of crystallization or melting at any temperature shown. Additional observations on heating this specimen were extended to +100° C (not shown in Figure 5), with no evidence of crystallization or melting or other transition evidenced by change of slope. The marked linearity shown

when crystallization is absent is contrasted with the curvature existing in measurements of expansion on X-6160 below the crystallization range. This result may indicate that the amount of crystalline material is varying, with consequent curvature of the graphs, over a considerable range of temperature.

The change in rate of expansion at the second-order transition is greater for X-6073 than for X-6160, and the transition occurs at a slightly higher temperature.

The data obtained have been used to calculate coefficients of linear expansion of silicone rubbers. It is to be emphasized that there is some doubt concerning the reliability of the results, since no special precautions were taken to avoid possible tilting of the specimens as discussed by Saunders[9] and because the slopes of expansion curves were obtained graphically from single runs in most instances. The coefficients of expansion are given in Table 1.

TABLE 1

COEFFICIENTS OF LINEAR THERMAL EXPANSION OF SILICONE RUBBERS

Silicone rubber	Temperature range (° C)	Heating or cooling	Coefficients of expansion per degree C: Below second-order transition	Immediately above second-order transition	Above crystallization or melting range
G. E. 9979G gum silicone n = 1.4040	−35 to 0	Heating	—	—	39×10^{-5}
G. E. 9979G gum silicone n = 1.4028	−35 to 0	Heating	—	—	40
	−120 to −100	Heating	—	18×10^{-5}	—
	−180 to −125	Heating	9×10^{-5}	—	—
Silastic 250	0 to −75	Cooling	—	—	22
	−120 to −102	Heating	—	25	—
	−180 to −120	Heating	7	—	—
Silastic X-6073	0 to −95	Cooling	—	16	—
	−116 to +100	Heating	—	17	—
	−180 to −116	Heating	3	—	—
Silastic X-6160	0 to −65	Cooling	—	—	24
	−35 to 0	Heating	—	—	25
	−120 to −90	Heating	—	11	—
	−180 to −120	Heating	4	—	—

It will be noted that the gum silicones have very high coefficients of expansion. The coefficient of cubical expansion of such isotropic material would be about 120×10^{-5} per degree C between −35° and 0° C, which is as large as that of many organic liquids.

The coefficients of expansion of the other silicone rubbers are lower, as expected from the fact that they all contain fillers that reduce the coefficients. The coefficients of these rubbers observed below the second-order transition temperature are approximately 15 to 35 per cent of the corresponding values above the transition.

SUMMARY

In the course of an investigation to determine which rubbers might be suitable for use at low temperatures, interferometric measurements of the length-temperature relationships of silicone rubbers have been made. Crystallization was found between −60° and −67° C in Dow-Corning Silastic X-6160 and in General Electric 9979G silicone rubber, the latter of which contains no filler. Crystallization between −75° and −85° C was found in Silastic 250. Melting occurred over a range of temperature above the temperature of crystallization. The volume change on crystallization varied from 2.0 to 7.8 per cent. No

crystallization or melting phenomena were observed in Silastic X-6073 between −180° and +100° C. All types of silicone rubber exhibited a second-order transition at about −123° C, the lowest temperature at which such a transition has been observed in a polymer. The coefficient of linear thermal expansion of silicone rubbers containing no filler was found to be about 40 × 10^{-5}/degree C between −35° and 0° C.

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SIMPLE METHOD FOR DETERMINING THE DYNAMIC COEFFICIENT OF FRICTION OF VULCANIZED RUBBER *

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INTRODUCTION

The determination of the coefficient of friction of rubber as a standard laboratory test has up till now received relatively little attention[1], though many experiments are described in the literature.

In the following, an apparatus is described which allows sufficiently accurate measurements of this coefficient at low speeds by means of a simple extension of the ordinary dynamometer design for tensile testing.

EXPERIMENTAL

The apparatus is shown schematically in Figures 1, 2, and 3. Two molded cylindrical rubber test-wheels of 100 and 80 mm. outer and inner diameter, respectively, and 10 mm. breadth[2], are clamped on a massive steel cylinder whose central diameter measures 80 mm. The total weight pressing on the rubber wheels may be varied. In the experiments described, this weight is 4.05 kg.; the contact area about 2 sq. cm. for a tread mix of the normal hardness of about 60 (Shore A). This corresponds to a load of about 2.0 kg. per sq. cm., which value was chosen for practical reasons. The wheels are pulled over the test surface by a cord attached to the moving clamp of the dynamometer and running over several pulleys. By changing the number of pulleys, the speed of the dynamometer may be multiplied to give an increased speed to the set of test-wheels; in this way considerable variation in speed is possible.

Around the central part of the steel cylinder two cords are wound, and these are fastened to an axis A. By turning axis A, the length of the cords relative to each other is changed so as to adjust the direction of the wheel system over the test surface. This is placed on a board fixed to the dynamometer frame on one end and supported at the other end.

The cords run over pulleys attached to the dynamometer in such a manner as to give readings equal to twice the tension in the cords.

By one complete turn of the wheels there would be a displacement of $2\pi r_2$ cm. (Figure 3). The cords allow a displacement of only $2\pi r_1$ cm., so there is a certain amount of slip as the wheels are pulled to the left. In the case under review, the slip is about 25 per cent of the actual displacement.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 26, No. 4, pages 281–287, December 1950. This paper is Communication No. 129 of the Rubber Foundation.

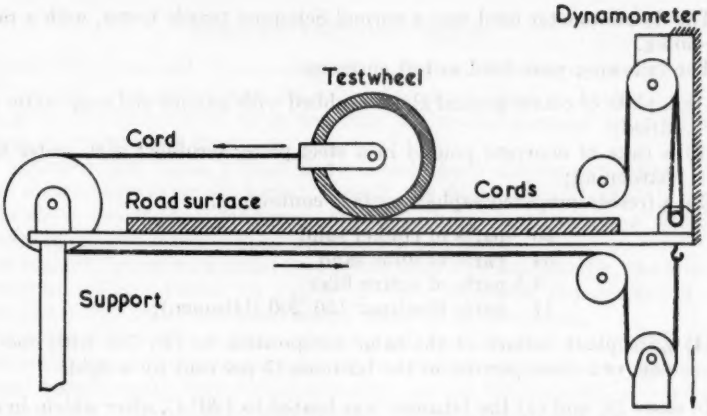

FIG. 1.—Side view of the assembly for measurement of the coefficient of friction.

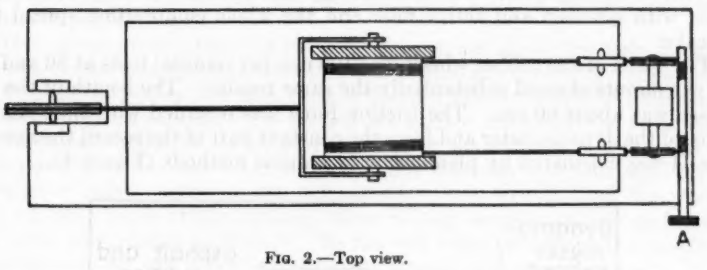

FIG. 2.—Top view.

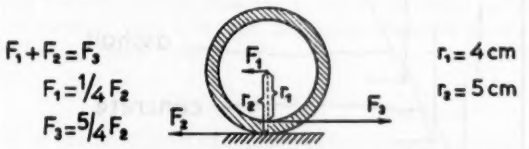

FIG. 3.—System of forces active during the friction test.

From Figure 3 it is obvious that the measured force F_3 is related to the frictional force F_2 by the formula:

$$F_3 = \frac{r_2}{r_1} F_2$$

$$\text{in our case } F_3 = \frac{5}{4} F_2$$

In the dynamometer twice the tension in the cord, F_3, is recorded. As the load is 4 kg., the coefficient of friction is

$$f = \frac{F_2}{4} = \frac{4/5 \times F_3}{4} = \frac{1 \times D}{10} \text{ (} D \text{ = dynamometer reading in kg.)}^3.$$

The dynamometer used was a normal Schopper tensile tester, with a range of 0–50 kg.

The following were used as test surfaces:

(1) a plate of coarse ground glass scrubbed with pumice and soap water and dried;

(2) a cake of concrete poured in a steel plate, scrubbed with water after hardening;

(3) a freshly prepared asphalt surface containing:

50 parts of clinker sand
34 parts of dune sand
4.5 parts of active filler
11 parts Shellspar 150/200 (bitumen);

(4) an asphalt surface of the same composition as (3), but with one-half part of rubber powder in the bitumen (5 per cent by weight).

In cases (3) and (4) the bitumen was heated to 120° C, after which, in case (4) the rubber powder (Mealorub prepared from latex) was added to the mix, and stirred for one hour. The mineral aggregate, heated to 140° C, was then mixed with bitumen and active filler and the whole composition spread to a flat cake.

The speed of the rubber wheels was 100 cm. per minute; tests at 80 and 120 cm. per minute showed substantially the same results. The length of the test surface was about 80 cm. The friction force was recorded with the standard device of the dynamometer and from the constant part of the record the average force D was calculated by planimetric or graphic methods (Figure 4).

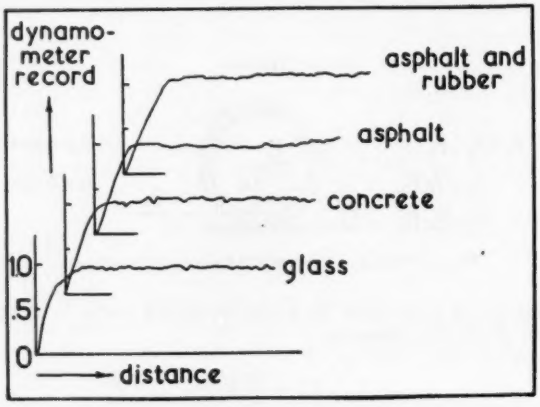

FIG. 4.—Specimen of dynamometer records.

The same set of samples was measured twice or three times on the same surface, and a second set was measured in some cases. The values given are averages of these runs, the value of each run in its turn being an average of the force during the time of the test. The average error of the measurement is about ±2 per cent when clean surfaces are used.

For tests on wetted surfaces, the surface sample was placed in a shallow container and repeatedly wetted by pouring ample quantities of tap water on it.

RESULTS AND DISCUSSION

About twelve natural rubber compounds, three GR-S compounds and two "cold" rubbers were tested, and the values found are listed in Tables 1 and 2, which give in a number of cases not only the overall-average but also the averages of the separate runs.

It appears from Table 1 that there is not much difference between the several natural-rubber types tested, though the Statex-K and H.P.C. compounds show the highest measured values. There is, however, a definite difference in friction when various surfaces are compared.

The highest figures were noted for asphalt with a rubber powder, the lowest for concrete. The addition of rubber powder increased the coefficient of friction of the bitumen in all cases tested under these conditions.

The natural-rubber pure gum vulcanizate did not show a particularly high friction coefficient; a mix containing about 25 per cent of cyclorubber, however, exhibited exceptionally high values especially on the bitumen-rubber surface. On wetting, the high coefficient disappeared. This is shown in Table 2.

In Table 2 a comparison between the different rubber types used for tread mixes is also made. Here relatively little difference appears between the various types of polymers used.

Table 1 demonstrates that the natural-rubber tread shows the highest peak value, but on the average does not differ much from the synthetic compounds. Even with the natural-rubber tread mix or flooring as a surface, about the same value is found as on asphalt. On wetting the surface the coefficient of friction was lowered only about 10 per cent for the bituminous surfaces. In the case of ground glass there was not much difference, but concrete with four out of five rubbers gave higher values on the wet sample. It is possible that the water carries off loose parts of the surface; these rollong between rubber and road would lower the friction coefficient. In the wet state the bituminous surface with rubber powder was superior to bitumen alone in all cases measured. It is surprising to see in the experiment that the presence of water has so small an influence on the friction. This, however, has been observed before in case of clean surfaces wetted by clean water[4]

CONCLUSIONS

Measurements of the coefficient of friction at low speeds may be carried out with a simple device attached to the tensile tester for rubber. The various rubber types could not be arranged in a definite order of their coefficients of friction from the results given in the tables, but the four surfaces showed persistent differences when tested under the conditions described here. Wetting with clean tap water did not appreciably lower the coefficient of friction.

In all tests but one (wet and dry), the asphalt-rubber surface showed a higher friction value than the corresponding asphalt surface. Simplicity of method and instrument are points in favor of its use for friction measurements of rubber.

SUMMARY

A method for measuring the coefficient of friction at low speeds by means of a normal dynamometer for rubber testing is described. To this end a couple of molded rubber wheels are pulled over a piece of roadlike surface. At the same time the wheels are forced to rotate with a speed nonconcordant with the linear speed on the surface, so that a certain amount of friction occurs. The force

TABLE I

COEFFICIENT OF FRICTION FOR NATURAL RUBBER TREAD COMPOUNDS

Wheels of 10 cm. diameter — 25% friction — Velocity 100 cm. per min. — Indentation 0.20 mm. — Thickness of cord 0.70 mm.

Compound No.	2879	2878	2877	2874
Polymer	N.R.	N.R.	N.R.	N.R.
Carbon black	H.P.C.	H.P.C.	M.P.C.	E.P.C.
Acceleration	M.B.T.	Santocure	M.B.T.	Santocure
Hardness (Shore A, Durometer units)	67	71	65	73
Coefficient of friction on				Average (Separate runs)
Ground glass	1.01	1.00	0.87	1.97 —
Concrete	0.98	1.08	1.00	1.02 —
Bitumen with rubber powder	1.12	1.33	1.05	1.15 (1.16–1.16–1.13–1.12–1.13–1.12)
Bitumen	1.04	1.13	1.04	1.07 —
Rubber tread vulcanizate	—	—	—	1.61 (1.14–1.17)
Wetted surfaces			Average (separate runs)	Average (Separate runs)
Ground glass	—	—	0.97 (0.97–0.99–0.95)	0.94 (0.94–0.93)
Concrete	—	—	1.07 (1.08–1.07–1.07)	0.97 (0.97–0.98–0.97)
Bitumen + rubber	—	—	1.08 (1.09–1.07)	1.03 (1.02–1.05–1.01)
Bitumen	—	—	0.98 (0.98–0.97)	0.95 (0.94–0.95)

Compound No.	2940	2941	2942	2943	2944	2945
Polymer	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
Carbon black	RF	RF	RF	RF	RF	RF
Acceleration	Santocure	M.B.T.	Santocure	M.B.T.	Santocure	M.B.T.
Hardness	68	70	74	72	72	72
Coefficient of friction on						
Ground glass	1.03 (1.06–1.01)	0.95 (0.97–0.92–0.95)	0.96 (0.96–0.96)	0.91 (0.90–0.91)	0.94 (0.92–0.96–0.93)	0.90 (0.91–0.87–0.91)
Concrete	1.20 (1.20–1.21)	1.08 (1.07–1.08)	1.09 (1.09–1.10)	1.04 (1.02–1.06)	1.05 (1.04–1.05–1.06)	1.02 (1.01–1.01–1.05)
Bitumen with rubber powder	1.40 (1.40–1.40)	1.33 (1.30–1.32–1.37)	1.27 (1.26–1.22–1.30)	1.28 (1126–1.27–1.32)	1.22 (1.22–1.22)	1.23 (1.21–1.26)
Bitumen	—	1.15 (1.12–1.17–1.15)	1.09 (1.07–1.08–1.12)	1.12 (1.07–1.10–1.17)	1.12 (1.10–1.11–1.12)	1.06 (1.05–1.06–1.09)

The values between brackets are the figures for the separate runs from which the averages have been calculated.

TABLE II

COEFFICIENT OF FRICTION

Comparison of different polymers in tread mixes

Compound No. Polymer Carbon black (filler) Accelerations	2754 Cold rubber M.P.C. Santocure	2726 Cold Rubber U E.P.C. Santocure	2727 GR-S RF Santocure-Tuads	2630 GR-S E.P.C. Santocure-Tuads	2753 GR-S M.P.C. Santocure-Tuads	227 N.R. pure gum — M.B.T.S., D.P.G.	2695 N.R. Cyclorubber M.B.T.S., D.P.G.
Hardness (Shore A, Durometer units)	60	67	56	60	62	39	60
Coefficient of friction on							
Ground glass	0.95	0.91	1.08	0.94	1.06	0.91	0.91
Concrete	1.06	1.03	1.03	1.02	1.04	0.95	1.07
Bitumen + rubber powder	1.14	1.17	1.15	1.23	1.24	1.18	1.54
Bitumen	1.05	1.21	1.07	1.11	1.09	1.18	1.28
Rubber flooring or tread vulcanizate	—	—	—	—	ca. 1.00–1.10	—	—
Wetted surfaces							
Ground glass	1.06	—	1.02	—	0.97	0.93	0.90
Concrete	1.11	—	1.07	—	1.08	1.06	0.97
Bitumen with rubber powder	1.07	—	1.11	—	1.10	1.10	0.99
Bitumen	0.92	—	1.04	—	0.99	1.08	0.92

necessary to turn the wheels over the surface is recorded on the dynamometer; the average is proportional to the average coefficient of friction.

Preliminary experiments were carried out to prove the usefulness of the apparatus. A number of compounds of natural rubber, GR-S, and "cold" rubber were tested on four surfaces: asphalt, asphalt with rubber, concrete, and ground glass. Although the apparatus allows variation of load and of speed, the experiments were carried out at a speed of 100 cm. per minute and only with a load of 4 kilograms.

On dry surfaces, the highest coefficient of friction was found with a natural-rubber compound on an asphalt material in which rubber powder had been dispersed. With most rubbers this surface showed a somewhat higher coefficient of friction than did the asphalt without rubber-powder, which in turn was better than the other two surfaces. On the average there was little difference between the various rubber compounds, though natural rubber seemed to yield the highest values. Natural-rubber pure gum compound did not show higher values than the carbon black mixes, but a vulcanizate with cyclorubber instead of carbon black was definitely better.

REFERENCES

[1] Dawson and Porritt, "Rubber, Physical and Chemical Properties", 1935, p. 381.
[2] With smaller test wheels (40 × 50 mm. diameter, 10 mm. broad) measurements with 3-kg. and 4-kg. pressure were carried out, but the results were less accurate than with the larger wheels.
[3] In the actual calculation the thickness of the cord and the compression of the wheels are accounted for. The thickness of the cord was 0.70 mm. and the deformation of the rubber 0.15–0.17 mm. For most tread mixes these corrections are of the order of 1 per cent of the measured value.
[4] F. L. Roth, *et al.* *J. Research Natl. Bur. Standards*, **28**, 439 (1942); RUBBER CHEM. & TECHNOL. **16**, 155 (1943).

PLASTIC YIELD OF BUTADIENE-STYRENE AND ISOPRENE-STYRENE EBONITES *

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INTRODUCTION

As butadiene-styrene copolymer ebonites have been found to resist plastic deformation at elevated temperatures better than natural rubber ebonites[1], experiments were made to determine how this property depends on the butadiene/styrene ratio, and an isoprene-styrene copolymer was included to show the effect of replacing butadiene by isoprene.

The rubbers examined are listed in Table 1. Mixes of 68:32, and in some cases also 77:23, rubber: sulfur ratio were press-vulcanized for 3, 5, and 9 hours at 155° C. In the Buna-SSE mix, 5 per cent of coumarone resin (V-100) had to be added to assist processing. Plastic yield temperature was determined by the R.A.B.R.M. torsion method[2], with the temperature rising uniformly at 50° C per hour; "yield temperature" is the intercept, on the temperature axis, of the steeply rising part of the temperature/yield curve.

DISCUSSION OF RESULTS

Curves of yield temperature plotted against vulcanizing period were of three general types, of which examples are given in Figure 1.

	68:32 Mix	77:23 Mix
(1) Flattening beyond 4 or 4½ hours	natural rubber, isoprene-styrene	—
(2) Rising higher than (1) but flattening at 5.5 or 6 hours	Buna-SS, Darex, Hycar-EP	—
(3) Rising continuously	Buna-S, Buna-SIII, Buna-SSE, GR-S	Buna-SSE,* Buna-SS, Darex, Hycar-EP

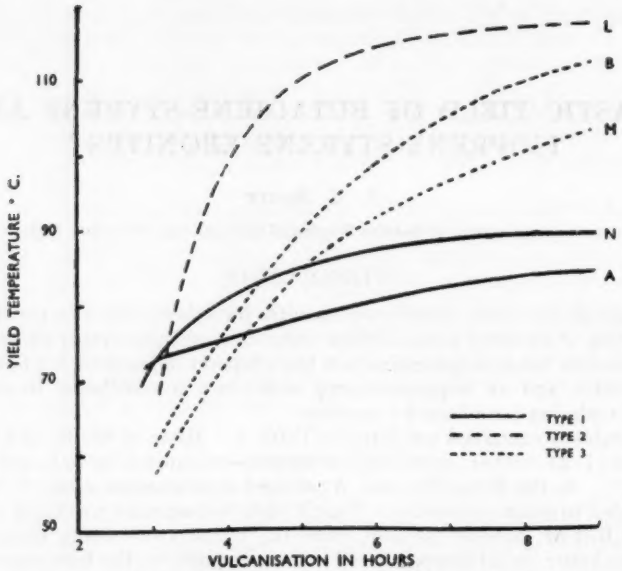
* Intermediate between (2) and (3).

The shape of the curve bears no obvious relation to the nature of the polymer, except that both those containing isoprene give type (1).

The optimum vulcanization was determined by plotting the yield at 100° C against the vulcanizing period, the optimum being taken as the period beyond which the yield remained substantially constant (this has been shown by previous R.A.B.R.M. work to be one of the best methods of fixing optimum vulcanization for GR-S ebonites). Where the vulcanization/yield temperature curve was of type (1) or (2), the beginning of the flat could be taken as an additional indication of optimum, and the periods so deduced agreed approximately with those deduced from the yield at 100° C.

Table 1 gives the optimum vulcanizing period and the corresponding yield temperature.

* Reprinted from the *Journal of Rubber Research*, Vol. 19, No. 12, pages 128–130, December 1950.



A = Natural Rubber (68:32)
L = Hycar-EP (68:32)
N = Isoprene-styrene copolymer (68:32)
B = GR-S (68:32)
M = Hycar-EP (77:23)

FIG. 1.—Change of plastic yield temperature with vulcanization.

Increasing the styrene content of the butadiene-styrene copolymers does not consistently affect the optimum vulcanizing period of the 68:32 mix, but the yield temperature at optimum cure increases progressively and reaches figures some 30° C above that for natural-rubber ebonite. It seems probable that the same would be true of isoprene-styrene copolymers. Replacing butadiene by isoprene lowers the yield temperature (cf. Bunas SIII and S with the isoprene-styrene copolymer).

TABLE 1

Polymer*	Styrene (%)	68:32 Mix Optimum (hours)	68:32 Mix Yield temp. (° C)	77:23 Mix Optimum (hours)	77:23 Mix Yield temp. (° C)
Bunas 85 and 115†	0	5	85	—	—
GR-S (type CC)	25	5	90	—	—
Buna-SIII	28	5	92	—	—
Buna-S	29	7	93	—	—
Buna-SSE	42	5	102	5½	99
Darex-2	44	5	101	7	103
Buna-SS	45	5¼	109	9	99
Hycar-EP	46	5	110	7	96
Natural rubber	0	5	90	—	—
Isoprene-styrene (GR-S-XP4)	28	4¾	84	—	—

* All the lettered Bunas were samples obtained from Germany in 1945.
† Data of Scott[1].

Reducing the sulfur content of the mix generally delays the optimum and somewhat reduces yield temperature.

In the 68:32 mix, the butadiene-styrene copolymers mostly reach optimum in the same time as natural rubber, and other R.A.B.R.M. investigations confirm this. The view at one time held[3], that butadiene-styrene copolymers vulcanize more slowly (in an ebonite mix) may have arisen from the fact that the yield temperature continues to rise beyond the optimum much more steeply than with natural rubber.

Determinations of free sulfur on the Darex and Buna-SS ebonites showed that the combined sulfur may correspond to more than 1 atom, *e.g.*, as much as 1.4 atoms, per double bond, *i.e.*, per butadiene molecule. This is true also of natural rubber ebonites[4]. To obtain the full benefit of the superior heat resistance of butadiene-styrene copolymer ebonites, the proportion of sulfur should correspond to more than 1 atom per butadiene molecule; for natural rubber the best plastic-yield resistance is obtained with nearly 1.2 atoms per isoprene[4], which would correspond to 52 parts of sulfur per 100 of a 75:25 butadiene-styrene copolymer. It does not, of course, follow that this would give the best values for other properties also.

SUMMARY

In unloaded ebonites made from butadiene-styrene copolymers, the resistance to plastic deformation at elevated temperatures is better the higher the styrene content of the copolymer, at least up to 46 per cent. An isoprene-styrene copolymer ebonite has poorer plastic-yield resistance than a corresponding butadiene-styrene ebonite. All the styrene-containing copolymers, however give ebonites more heat-resistant than natural rubber ebonite, the best giving yield temperatures 30° C above the latter. To attain the best plastic-yield resistance in butadiene-styrene ebonites, the amount of sulfur added should correspond to more than 1 atom (*e.g.*, 1.2 or even 1.4 atoms) per butadiene molecule.

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[2] Church and Daynes, *J. Rubber Research* **8**, 41 (1939).
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[4] Scott, *J. Rubber Research* **17**, 170 (1948).

DETERMINATION OF UNSATURATION OF BUTYL RUBBERS AND CERTAIN BRANCHED OLEFINS *

IODINE MONOCHLORIDE METHOD

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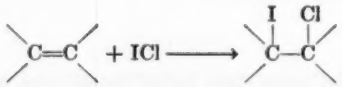
A reliable and convenient method for the determination of unsaturation of hydrocarbon polymers and of olefins can generally be based on the addition of iodine monochloride to the carbon-to-carbon double bond. The reaction is represented as follows:



(1)

The procedure usually consists in adding an excess of iodine monochloride to the solution of unsaturated compound and, after a suitable reaction period, determining by titration the amount of iodine monochloride remaining. Although the iodine monochloride method yields accurate results for most olefins and polymers, it yields high results for certain olefins and polymers that are branched in the neighborhood of the double bond. A number of such compounds have been cited in the literature: 3-ethyl-2-pentene[1]; trimethylethylene and limonene[2]; isobutylene dimers, trimers, and tetramers[3]; pinene, dipentene, and α-terpineol[4]; dihydromyrcene and squalene[5]; other branched olefins[6]; and Butyl rubbers[7]. Other examples are given herewith.

In the reaction of iodine monochloride with highly branched olefins and polymers, large amounts of acid and iodine are formed in the reaction mixture, indicating the occurrence of side reactions. The high results in the determination of unsaturation and the formation of iodine and acid are often ascribed to substitution, although it has for some time been apparent that substitution cannot account quantitatively for the observed results.

Substitution may be represented as follows[8]:

(2)

(3)

Reaction 2 indicates that one mole of halogen is reduced for each hydrogen atom of the olefin that is replaced. Reaction 3 has the effect of converting iodine monochloride to free iodine without affecting the total iodometric titer of the reaction mixture. Inasmuch as one molecule of acid is formed for every mole of halogen reduced by substitution, it would be expected that the experi-

* Reprinted from *Analytical Chemistry*, Vol. 22, No. 8, pages 995–1001, August 1950. The present address of T. S. Lee is the University of Chicago, Chicago, Illinois.

mental results in the determination of unsaturation could be corrected for substitution by application of the equation:

$$a = b - c \tag{4}$$

where a is the unsaturation (expressed as the number of moles of double bonds originally present), b is the decrease in the total iodometric titer (expressed as moles of halogen), and c is the number of moles of acid formed. [The value of c can be found by titrating the acid formed in the reaction mixture[9]. Inasmuch as the molar amounts of acid and of iodine formed by substitution are equal[8], the value of c alternatively can be found by titrating the free iodine in the reaction mixture.]

It has been observed, and is also evident from the data and discussion below, that Equation 4 yields a low value for the unsaturation of highly branched olefins and polymers[10], and, indeed, even for many polymers that are not highly branched[8]. This means that the amount of acid (and of iodine) formed in the reaction of iodine monochloride with branched olefins and polymers is greater than can be accounted for by substitution.

Another side reaction, "splitting out" has been assumed to occur when halogens react with olefinic substances[11]. It is thought that the halogen first adds to the double bond and that subsequently a molecule of hydrogen halide splits out. It seems especially probable that the splitting-out reaction would occur when iodine monochloride is added to highly branched olefins and polymers, inasmuch as the addition products undoubtedly possess steric strain. Indeed, it was found impossible to construct steric models of the iodine monochloride addition products of certain branched olefins, owing to the large sizes of the halogen atoms and of alkyl groups. Those branched olefins which yield high results by the iodine monochloride method appear, from consideration of the models, to be unable to accommodate simultaneously an iodine and a chloride atom without considerable steric strain. Thus, it would seem reasonable that if these olefins add iodine monochloride momentarily, the resulting addition products would be unstable and would lose or split out hydrogen iodide or hydrogen chloride. On the basis of evidence given below it is concluded that only hydrogen iodide and no hydrogen chloride splits out. In general, the splitting-out reaction is presumed to be represented as follows:

$$\begin{array}{cccc} & \mathrm{I} & \mathrm{Cl} & \\ & | & | & \\ -\mathrm{CH}- & \mathrm{CH}- & \longrightarrow & -\mathrm{CH}=\mathrm{C}- \end{array} \begin{array}{c} \\ \\ \\ \mathrm{Cl} \\ | \\ \end{array} + \mathrm{HI} \tag{5}$$

and is followed by the reaction of hydrogen iodide with iodine monochloride (Reaction 3). [It is possible that the splitting out of hydrogen iodide forms bonds of the type:

$$-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}(\mathrm{Cl})-$$

as well as bonds of the type $-\mathrm{CH}=\mathrm{CCl}-$. The former bonds would be expected to react more rapidly with iodine monochloride than the latter. However, experimental evidence indicates that no highly reactive double bonds are formed as a result of splitting out.]

The double bond created by Reaction 5 would be expected to add iodine monochloride only slowly because of the retarding inductive effect of the chlorine atom. Indeed, it is known that the double bonds in polychloroprene (Neoprene), which are of the type $-\mathrm{CH}=\mathrm{CCl}-$, add iodine monochloride only slowly[12].

As for the accuracy of the iodine monochloride method of determining unsaturation, the splitting out Reactions 5 and 3 would not affect the total iodometric titer and, therefore, would not directly affect the accuracy of the results. However, addition of iodine monochloride to the newly created double bonds would cause high results. In general, the greater the extent of splitting out, the higher the results due to this source of error.

The interpretation given above (splitting out and addition of iodine monochloride to the newly created double bonds) conforms to the results of a study of the reaction of iodine monochloride with a number of branched olefins and with Butyl rubbers. The interpretation also led to a modified iodine monochloride method which yields reliable results for highly branched olefins and polymers.

EXPERIMENTAL

Materials used.—Iodine monochloride stock solutions were prepared by dissolving Eastman practical grade iodine monochloride in analytical reagent grade carbon tetrachloride. The exact titers of the iodine monochloride solutions were determined by titration with thiosulfate solution. Small amounts of iodine trichloride, which sometimes occurs as an impurity in the Eastman iodine monochloride, do not interfere in the recommended procedures, described below. However, in the experiments in which free iodine is determined (experiments of Figures 1 to 3, 6, and 7), it is necessary to convert any iodine trichloride present in the stock solution to iodine monochloride by the addition of the proper amount of iodine. The amount of iodine trichloride originally present was determined by titration of a portion of the stock solution with iodide solution, as described elsewhere[8].

The olefins used were obtained, with one exception, from the National Bureau of Standards and were stated to be at least 99.9 per cent pure. A sample of 3-methyl-2-pentene of unknown purity was also used.

Samples of unvulcanized Butyl rubber[13] were purified in the authors' laboratory as follows: Five grams of rubber were dissolved at room temperature in 500 cc. of *n*-hexane. The solution was filtered through glass wool to remove any suspended impurities and any gel present. The rubber was precipitated by adding the solution slowly to 2 liters of methanol. During the addition the methanol was stirred vigorously with a motor-driven stirrer. The precipitated rubber was collected and dried for 24 hours at room temperature in a vaccuum desiccator. The above procedure effectively removes the inhibitor (generally phenyl-2-naphthyl-amine) which is added to Butyl rubber to retard autoxidation.

Investigation of reaction of iodine monochloride with olefins and polymers.—Reaction mixtures were prepared as follows:

A carbon tetrachloride solution of the olefin was added to a volumetric flask, a solution of iodine monochloride in carbon tetrachloride was added, and the mixture was diluted to the mark with the same solvent. After varying reaction periods aliquot portions of the reaction mixture were removed and analyzed for total iodometric titer by titration with thiosulfate, amount of free iodine by titration with iodate in a hydrochloric acid medium, and amount of acid by the McIlhiney method (removal of the excess iodine monochloride and iodine with neutral aqueous iodide and thiosulfate solutions, followed by addition of iodate and titration of the liberated iodine with thiosulfate). The procedures for these determinations are described elsewhere[8]. The amount of iodine monochloride remaining was found by subtracting the amount of free iodine from the total iodometric titer.

The results of the experiments are summarized in Figures 1 to 3, 6, and 7. The amounts of free iodine and of acid formed were corrected for the small amounts of these components present initially in the iodine monochloride stock solutions.

Recommended procedure for determination of branched olefins.—A stock solution of olefin is prepared by adding a known weight of the sample to a volumetric flask and filling the flask to the mark with reagent grade carbon tetrachloride. If the sample is volatile, it should be weighed in a Victor Meyer bulb, and the bulb broken with a stirring rod under the surface of the carbon tetrachloride. Loss of olefin by volatilization may further be minimized by cooling the carbon tetrachloride to 0° before breaking the bulb. The concentration of olefin in the stock solution should be 0.01 to 0.03 *M* for best results. Twenty-cc. portions of the olefin stock solution are added to a series of five to eight iodine flasks, each containing 40 cc. of carbon tetrachloride. Varying amounts of 0.05 *M* iodine monochloride solution in carbon tetrachloride are added to the flasks. For convenience the iodine monochloride solution may be dispensed from a buret (no stopcock grease!). The amounts of iodine monochloride used should be such as to provide an initial molar ratio of halogen to olefin or about 0.5 to 3 (see Figures 4, 5, 8, and 9). The iodine flasks are then stoppered and allowed to stand at room temperature for 1 hour, 40 cc. of 0.5 *M* aqueous acetic acid solution and 1 gram of potassium iodide are added, the mixture is shaken, and the liberated iodine is titrated with standard 0.05 or 0.1 *M* thiosulfate solution. Starch solution is added when the end point is approached.

To find the titer of the iodine monochloride, a blank reaction mixture containing no olefin is prepared and titrated in the same way as the sample reaction mixtures. Only one blank need be prepared for each series of sample reaction mixtures.

The total iodometric titer of each reaction mixture is found from the equation:

$$\text{Millimoles of halogen} = \frac{\text{ml. of thiosulfate} \times \text{normality of thiosulfate}}{2} \tag{6}$$

The decrease in total iodometric titer, expressed in millimoles of halogen per gram of sample and represented by d, for each reaction mixture is given by the expression:

$$d = \frac{(\text{millimoles of ICl added}) - (\text{millimoles of halogen remaining})}{\text{weight of sample in 20 ml. of stock solution}} \tag{7}$$

The calculated values of d are plotted against the initial ratio of halogen to olefin (expressed in any convenient units). An illustration of this plot is given in Figures 4 and 5. The value of d corresponding to the discontinuity in the curve is designated as d_d and is equal to the unsaturation of the sample (expressed as millimoles of double bonds per gram of sample).

If it is desired to express the unsaturation of the sample as iodine number (I.N.), the following relation can be used:

$$\text{I.N.} = d_d \times 25.38 \tag{8}$$

If it is desired to express the unsaturation of the sample as percentage of theoretical, the equation is:

$$\%\ \text{of theoretical} = d_d \times \frac{\text{M.W.}}{10} \tag{9}$$

where M.W. is the molecular weight of the olefin.

Recommended procedure for determination of unsaturation of Butyl rubbers.—The Butyl rubber is purified as described above. A stock solution is prepared by dissolving a weighed portion of the rubber in carbon tetrachloride at room temperature. The size of the sample should be chosen to yield a solution that is 0.005 to 0.02 *M* in double bonds, *i.e.*, in isoprene or butadiene units. The dissolution of the sample requires from several hours to a day, but may be hastened by putting the flask in a mechanical shaker[14].

Twenty-milliliter portions of the stock solution are added to a series of five to eight iodine flasks, each containing 20 cc. of carbon tetrachloride. (If the unsaturation of the Butyl rubber is low, 50- instead of 20-cc. portions of the stock solution may be used. In this case the concentration of double bonds in the stock solution may be as low as 0.002 *M*. No additional carbon tetrachloride should be added.) Varying amounts of 0.02 *M* iodine monochloride are added to the flasks. For best results the amounts of iodine monochloride added should correspond to initial molar ratios of halogen to double bonds varying between 0 and 3. The reaction mixtures are allowed to stand 1 hour in the glass-stoppered flasks and then the iodometric titer is determined as described above. The decrease in total iodometric titer is calculated for each reaction mixture from Equation 6. The value of d is plotted against the initial ratio of iodine monochloride to olefin (expressed as millimoles of halogen per gram of sample). This plot is illustrated in Figures 8 and 10. The value of d corresponding to the discontinuity in the curve (d_d) is equal to the unsaturation of the polymer expressed in millimoles of double bonds per gram. The relation between d_d and the mole per cent of copolymerized isoprene or butadiene is:

$$\text{Mole } \% \text{ isoprene or butadiene} = d_d \times 5.61 \qquad (10)$$

Equation 10 is not exact, but is based on the assumption that the average molecular weight of the monomer units in Butyl rubbers is 56.1, the molecular weight of isobutylene itself[4]. Equation 10 is sufficiently accurate for all practical work, provided that the Butyl rubber does not contain more than 5 per cent isoprene or 10 per cent butadiene (see below). The relation between d_d and the iodine number of the rubber is given in Equation 8.

REACTION OF IODINE MONOCHLORIDE WITH DIISOBUTYLENES

2,4,4-Trimethyl-1-pentene(diisobutylene-1) and 2,4,4-trimethyl-2-pentene (diisobutylene-2) were chosen as representative highly branched olefins. The experimental results of the reaction of iodine monochloride with these two olefins are shown in Figures 1 to 3. In the experiments of Figure 1 the initial molar ratio of iodine monochloride to olefin is 1.5. It is seen that the decrease in total iodometric titer is 1.0 mole of halogen per mole of olefin, the theoretical decrease expected for addition of iodine monochloride to an olefin. However, large amounts of iodine are formed in the reaction mixtures. The source of this iodine is not substitution, for substitution would be accompanied by a corresponding decrease in iodometric titer. Furthermore, when iodine monochloride was allowed to react with 2,4,4-trimethylpentane (hydrogenated diisobutylene) under the conditions of Figure 1, the decrease in iodometric titer was less than 0.01 mole of halogen per mole of hydrocarbon after a 4-hour reaction period—the substitution was practically negligible. It can be concluded that under the experimental conditions of Figure 1 the addition of iodine monochloride to the diisobutylenes is very rapid and that splitting out is also rapid. It can be seen from Figure 1 that the concentration of iodine monochloride in the reaction mixture after the initial stages of reaction was very

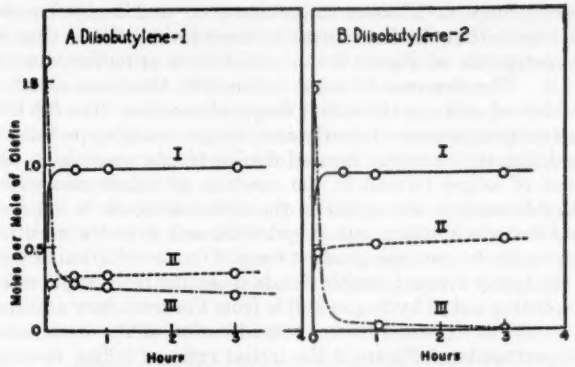


FIG. 1.—Reaction of diisobutylenes with iodine monochloride. Initial molar ratio of ICl to olefin 1.5, initial concentration of olefin 0.02 *M*, temperature 25° C, solvent CCl_4. I. Decrease in total iodometric titer (expressed as moles of halogen). II. Iodine formed. III. Iodine monochloride remaining.

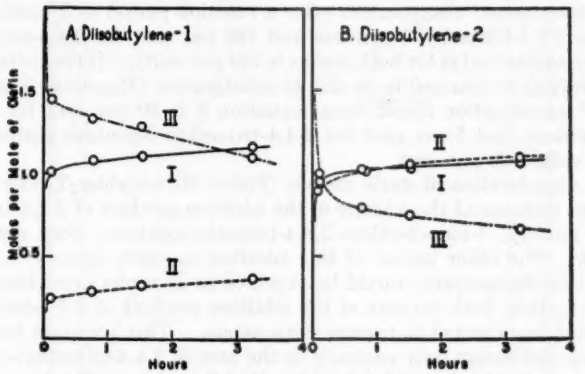


FIG. 2.—Reaction of diisobutylenes with iodine monochloride. Same conditions as in Figure 1 except initial molar ratio of ICl to olefin 3.0.

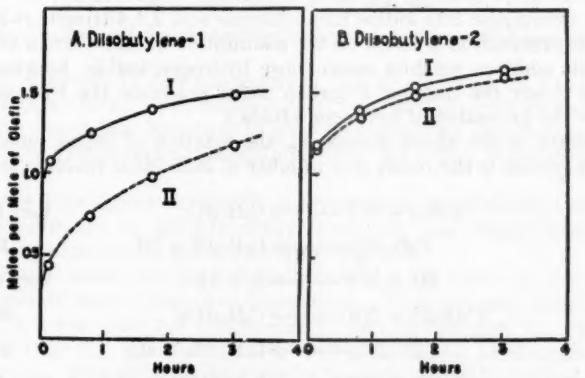


FIG. 3.—Reaction of diisobutylenes with iodine monochloride. Same conditions as in Figure 1 except initial molar ratio ICl to olefin 5.0.

small. Consequently, no addition to the newly created double bonds occurred. It is for this reason that the theoretical decrease in iodometric titer was found.

In the experiments of Figure 2 the initial ratio of iodine monochloride to olefin was 3.0. The decrease in total iodometric titer was about 1 mole of halogen per mole of olefin in the initial stages of reaction (0 to 0.5 hour). The total iodometric titer decreased slowly over longer reaction periods, indicating that slow addition to the newly created double bonds was taking place. The molar amount of iodine formed in the reaction of iodine monochloride with 2,4,4-trimethyl-2-pentene was equal to the molar decrease in iodometric titer; this indicated that the splitting out of hydriodic acid from the addition product is quantitative and also that the product formed by the addition of iodine monochloride to the newly created double bonds quantitatively splits out hydriodic acid. The splitting out of hydrogen iodide from the secondary addition product ($C_8H_{15}ICl_2$) would be expected from a consideration of the steric models.

In the experiments of Figure 3 the initial ratio of iodine monochloride to olefin was 5.0. The results are similar to the experiments of Figure 2 except that, as would be expected, the addition of iodine monochloride to the newly created double bonds is more pronounced. In the experiments of Figure 3 the apparent, uncorrected unsaturation after a reaction period of 3 hours was 150 per cent for 2,4,4-trimethyl-1-pentene and 160 per cent for 2,4,4-trimethyl-2-pentene (theoretical value for both olefins is 100 per cent). If the iodine formed in these reactions is assumed to be due to substitution (Reactions 2 and 3) the "corrected" unsaturation found from Equation 4 is 30 per cent for 2,4,4-trimethyl-1-pentene and 5 per cent for 2,4,4-trimethyl-2-pentene instead of the theoretical value 100 per cent.

From a consideration of steric models (Fisher-Hirschfelder-Taylor models), it is expected that one of the isomers of the addition product of 2,4,4-trimethyl-1-pentene, namely, 1-iodo-2-chloro-2,4,4-trimethylpentane, does not possess steric strain. The other isomer of this addition product, namely, 1-chloro-2-iodo-2,4,4-trimethylpentane, would be expected to be under great steric strain. In contrast to this, both isomers of the addition product of 2,4,4-trimethyl-2-pentene would be expected to possess steric strain. This accounts for the fact that splitting out occurs only partially in the case of 2,4,4-trimethyl-1-pentene but completely in the case of 2,4,4-trimethyl-2-pentene. (In regard to the addition products of 2,4,4-trimethyl-2-pentene, it is interesting to note that if 2-chloro-3-iodo-2,4,4-trimethylpentane is formed momentarily, it would be expected to decompose into iodine monochloride and 2,4,4-trimethyl-2-pentene again. This expectation is based on the assumption of steric strain and on the fact that this addition product cannot lose hydrogen iodide, because neither the number 2 nor the number 4 carbon atom possesses the hydrogen atom required for the formation of hydrogen idoide.)

In summary of the above discussion, the reaction of iodine monochloride with diisobutylenes is the result of a number of individual reaction steps:

$$C_8H_{16} + ICl \longrightarrow C_8H_{16}ICl \qquad \text{Very fast} \qquad (11)$$

$$C_8H_{16}ICl \longrightarrow C_8H_{15}Cl + HI \qquad \text{Fast} \qquad (12)$$

$$HI + ICl \longrightarrow I_2 + HCl \qquad \text{Very fast} \qquad (13)$$

$$C_8H_{15}Cl + ICl \longrightarrow C_8H_{15}ICl_2 \qquad \text{Slow} \qquad (14)$$

$$C_8H_{15}ICl_2 \longrightarrow C_8H_{14}Cl_2 + HI \qquad \text{Fast} \qquad (15)$$

$$HI + ICl \longrightarrow I_2 + HCl \qquad \text{Very fast} \qquad (16)$$

Reaction 11 represents rapid addition, Reaction 12 represents rapid splitting out of hydrogen iodide, Reaction 14 represents slow addition of iodine monochloride to newly created double bonds, and Reaction 15 represents splitting out of hydrogen iodide from the secondary addition product.

It was found, by determination of the acid in a number of the reaction mixtures, that the molar amount of iodine formed was in all cases substantially equal to the molar amount of acid formed. This result would be expected on the basis of the above scheme.

Consideration of Reactions 11 to 14 leads to the expectation that reliable results may be obtained in the determination of unsaturation of branched olefins if the appropriate excess of iodine monochloride over olefin is used. Thus, if the initial excess of iodine monochloride is small and if Reaction 12 is much

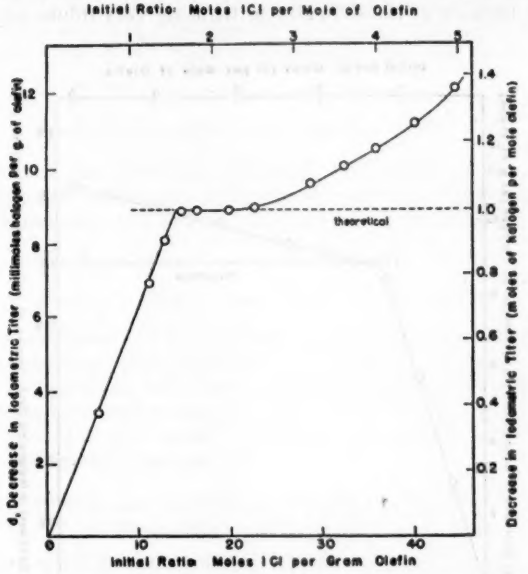


FIG. 4.—Determination of 2,4,4-trimethyl-2-pentene by recommended procedure.

faster than Reaction 14 but not nearly so fast as Reaction 11, the decrease in iodometric titer should be equivalent to the amount of olefin initially present. Under these conditions Reaction 11 goes to completion and Reactions 12 and 13 convert the excess iodine monochloride into free iodine, which does not react further.

In Figure 4 are shown the results of experiments in which the initial ratio of iodine monochloride to 2,4,4-trimethyl-2-pentene was varied from 0.6 to 5. The following conclusions are drawn from Figure 4.

If the initial molar ratio of halogen to olefin is less than 1.5, the decrease in total iodometric titer is less than theoretical. This indicates that the rate of Reaction 12 is less than but comparable to that of Reaction 11. Thus, if the ratio is less than 1.5, Reaction 11 and Reactions 12 and 13 compete for iodine monochloride. This explains why the iodine monochloride method sometimes yields low results in the determination of branched olefins[4].

If the initial molar ratio of halogen to olefin is between 1.5 and 2.5, the theoretical decrease in iodometric titer is obtained. This is reasonable on the basis of the discussion given above.

If the ratio is greater than about 2.5, the decrease in iodometric titer is larger than theoretical, due to Reaction 14.

When both the iodine monochloride and the 2,4,4-trimethyl-2-pentene were diluted without changing the ratio of the two reactants, the relative importance of Reaction 14 compared with Reaction 12 was diminished. This is to be expected, because Reaction 12 is presumably a first-order reaction while Reaction 14 is of higher order. As a result of this effect, values of unsaturation close to the theoretical value can be obtained when the reaction mixture is very dilute, even if the initial ratio of iodine monochloride to olefin is 4 or more. In general, it is not advisable, however, to carry out the determination of unsaturation at high dilution because of the difficulty in titrating very dilute solutions.

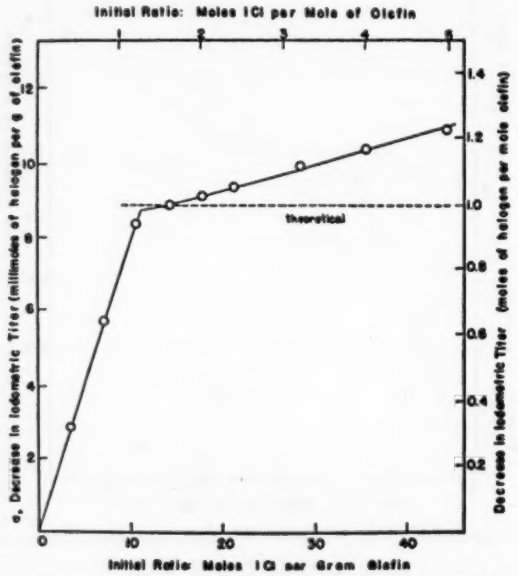


FIG. 5.—Determination of 2,4,4-trimethyl-1-pentene by recommended procedure

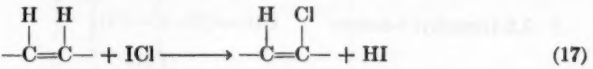
Experiments similar to those of Figure 4 were carried out in which 2,4,4-trimethyl-1-pentene was used instead of 2,4,4-trimethyl-2-pentene (Figure 5). It is seen that the theoretical decrease in iodometric titer is obtained only if the initial ratio of halogen is within certain narrow limits. This would be expected from the fact that the splitting out Reaction 12 is far from complete in the case of 2,4,4-trimethyl-1-pentene (whereas it is complete in the case of 2,4,4-trimethyl-2-pentene). Consequently, in the reaction of iodine monochloride with 2,4,4-trimethyl-1-pentene, the excess of iodine monochloride is not converted into free iodine even when the excess of iodine monochloride is small. On the other hand, Reaction 14 undoubtedly is not so rapid in the case of 2,4,4-trimethyl-1-pentene as in the case of 2,4,4-trimethyl-2-pentene. Consequently, if the

initial ratio of halogen to olefin is high—*e.g.*, 4 or 5—the decrease in total iodometric titer is not so large in the reaction of 2,4,4-trimethyl-1-pentene as in the reaction of 2,4,4-trimethyl-2-pentene.

As can be seen from Figures 4 and 5, a method for the determination of the diisobutylenes and similar branched olefins is the following: A number of reaction mixtures are prepared with varying ratios of iodine monochloride to olefin. After a suitable reaction period the decrease in iodometric titer of each reaction mixture is determined and the results are plotted as shown in Figures 4 and 5. The discontinuity in the curve corresponds to the unsaturation of the sample (see recommended procedure).

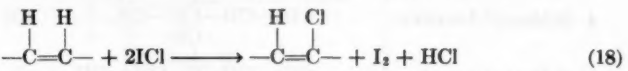
The procedure should also be applicable to a mixture of branched and unbranched olefins, as well as to the determination of terpenes[15].

The results given in Figures 1 to 5 show that iodine monochloride first adds to the double bonds and that subsequently hydrogen iodide splits out from the addition product. The direct reaction apparently does not occur. Reaction



(17)

17 is eliminated by the following reasoning. Inasmuch as the reaction of hydrogen iodide with iodine monochloride is very rapid (presumably much more rapid than Reaction 17) we can write, in place of Reaction 17,



(18)

In the case of a substance like 2,4,4-trimethyl-2-pentene, the addition product of which is completely unstable (see Figures 2,*B*, and 3,*B*), it would be expected from Equation 18 that if the initial ratio of iodine monochloride to double bonds was 1.5, the decrease in total iodometric titer would be only 1.5/2 or 0.75 mole of halogen per mole of double bonds. Actually, it was found (Figure 1,*B*) that the decrease in iodometric titer was 1.0.

REACTION OF IODINE MONOCHLORIDE WITH OTHER BRANCHED OLEFINS

To find which olefin structures cause splitting out, several branched olefins were allowed to react with iodine monochloride, and the amounts of free iodine formed after 0.1- and 1-hour reaction periods were determined. The results are given in Table I. The amount of splitting out is represented approximately by the amount of iodine formed in the first 0.1 hour[8], although splitting out may not be rapid in all cases. Moreover, slow addition of iodine monochloride to newly created double bonds may occur, resulting in further splitting out over an extended period of time. Addition to newly created double bonds causes the "apparent unsaturation" to be higher than theoretical. In Table I the "apparent unsaturation" in the uncorrected percentage of theoretical unsaturation found after a reaction period of 1 hour.

From Table I it is seen that no detectable splitting out occurs in the reaction of iodine monochloride with olefins that do not possess side alkyl groups. The extent of splitting out is also small for straight-chain olefins possessing only one side methyl group. Construction of steric models indicates that the addition products of these two types of olefins are not under steric strain. However, if additional alkyl groups are added to the α or β carbon atoms, steric strain

TABLE I

REACTION OF IODINE MONOCHLORIDE WITH OLEFINS AND POLYMERS
(Initial molar ratio of halogen to olefin 1.5, initial concentration of double bonds 0.02 *M*, solvent CCl_4, temp. 25° C)

Expt.	Olefin or polymer	Structure	Apparent unsaturation, %	Iodine formed, moles per mole of double bonds × 100: In first 0.1 hour	Iodine formed, moles per mole of double bonds × 100: In next hour
1	Unbranched olefins (1-octene, 1-pentene, *cis*-2-pentene, *trans*-2-pentene)	$RCH{=}CHR$ and $RCH{=}CH_2$	98–100	0–1	0–1
2	3,3-Dimethyl-1-butene	$CH_2{=}CH{-}C(CH_3)_2{-}CH_3$	98	0	0.2
3	2-Methyl-2-butene	$CH_3{-}C(CH_3){=}CH{-}CH_3$	—	0	0
4	3-Methyl-1-butene	$CH_2{=}CH{-}CH(CH_3){-}CH_3$	101	2.7	0
5	3-Methyl-2-pentene[a]	$CH_3{-}CH{=}C(CH_3){-}CH_2{-}CH_3$	98	5.5	6
6	2-Methyl-1-butene	$CH_2{=}C(CH_3){-}CH_2{-}CH_3$	106	7.7	2
7	2,4,4-Trimethyl-1-pentene	$CH_2{=}C(CH_3){-}CH_2{-}C(CH_3)_3$	108[b]	25[b]	4[b]
8	2,4,4-Trimethyl-2-pentene	$CH_3{-}C(CH_3){=}CH{-}C(CH_3)_3$	103[b]	90	13[b]
9	Isoprene Butyl rubber	———	—	29–42[b]	—
10	Butadiene Butyl rubber	———	—	8–11[b]	—

[a] Purity of sample of 3-methyl-2-pentene unknown.
[b] Initial molar ratio of iodine monochloride to double bonds 3.0.

usually results. The steric strain is reflected in the experimental data of experiments 7 to 10.

It can be concluded from Table I that the ordinary iodine monochloride method is reliable for determination of unbranched olefins or for branched olefins of the type used in experiments 2 to 5. It is not applicable for the more highly branched olefins or polymers of experiments 7 to 10.

REACTION OF IODINE MONOCHLORIDE WITH BUTYL RUBBERS

Butyl rubbers are copolymers of iosbutylene and either isoprene or butadiene. The amount of iosprene or butadiene in the copolymer is small, generally about 0.2 to 5 mole-per cent of the monomer units. The unsaturation

possessed by Butyl rubbers is presumably due entirely to the isoprene or butadiene units and consequently a method for determination of unsaturation provides a mean for determining these constituents.

Inasmuch as the structure of the isobutylene-isoprene copolymer (isoprene Butyl rubber) closely resembles that of the diisobutylenes, a large amount of splitting out would also be expected to occur in the reaction of iodine monochloride with isoprene Butyl rubber. Figures 6 and 7, which show the reaction of iodine monochloride with isoprene Butyl rubber, should be compared with Figures 1,*B*, and 3,*B*, respectively. It is seen that isoprene Butyl rubber and 2,4,4-trimethyl-2-pentene do indeed react in a very similar manner. The theoretical decrease in iodometric titer found in the experiment of Figure 6 indi-

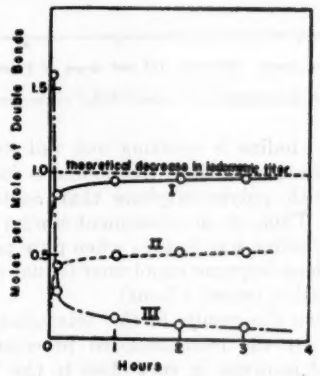


FIG. 6.—Reaction of isoprene Butyl rubber with iodine monochloride. Initial molar ratio of ICl to double bonds 1.5, initial concentration of polymer 5.61 grams per liter, initial concentration of ICl 0.00314 *M*. I, II, and III as in Figure 1.

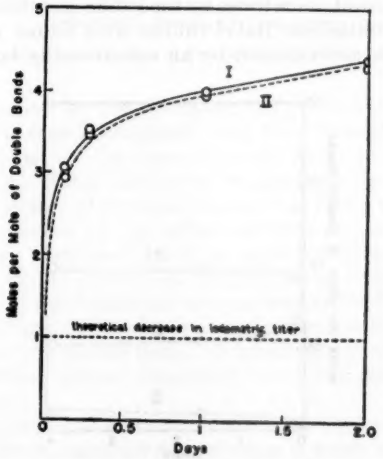


FIG. 7.—Reaction of isoprene Butyl rubber with iodine monochloride. Initial molar ratio of ICl to double bonds 11.0, initial concentration of polymer 2.46 grams per liter, initial concentration of ICl 0.025 *M*. I and II as in Figure 1.

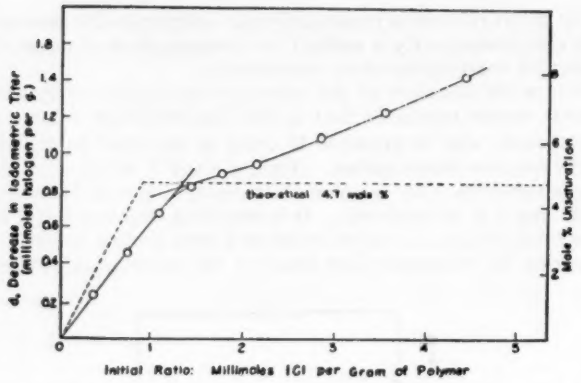


FIG. 8.—Determination of unsaturation of isoprene Butyl rubber by recommended procedure.

cates that the source of iodine is splitting out, not substitution. In further support of this supposition, very little free iodine is formed in the reaction of iodine monochloride with polyisobutylene that contains no copolymerized butadiene or isoprene. Thus, in an experiment similar to that of Figure 6 less than one tenth as much iodine was formed when pure polyisobutylene was substituted for the isobutylene-isoprene copolymer (equal weights of polymer used in each experiment, reaction period 1 hour).

In Figure 8 are shown the results of the determination of unsaturation of isoprene Butyl rubber by the recommended procedure. The unsaturation found, 4.6 mole-per cent isoprene, is very close to the "theoretical" value, 4.7 obtained by the perbenzoic acid method. The latter method is known to be reliable for this type of polymer and will be described in a subsequent publication. The value found from Figure 8 is also close to the value 4.9 found for the same sample at the Esso Laboratories by the iodine-mercuric acetate method[4].

The reaction of butadiene Butyl rubber with iodine monochloride would not be expected to be accompanied by an exceptionally large amount of split-

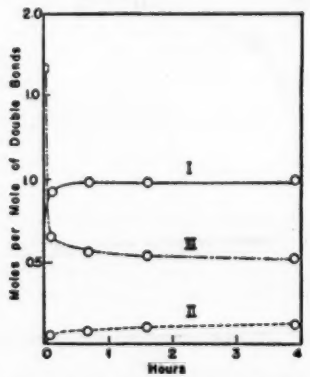


FIG. 9.—Reaction of butadiene Butyl rubber with iodine monochloride. Conditions similar to those of Figure 6. I, II, and III as in Figure 1.

ting out, inasmuch as the butadiene units in the copolymer do not contain side alkyl groups. Some splitting out can be expected, however, because of the proximity of the butadiene units to the highly branched isobutylene units.

Figure 9 shows the reaction of iodine monochloride with butadiene Butyl rubber. The conditions of this experiment are essentially the same as in the corresponding experiment with isoprene Butyl rubber (Figure 6). Comparison of Figures 6 and 9 shows that the amount of splitting out which occurs in the reaction of the butadiene copolymer is relatively small. From Figure 9 it can also be seen that the decrease in iodometric titer is nearly theoretical, even though a relatively large excess of iodine monochloride is present throughout the reaction period.

In Figure 10 are shown the results of the determination of unsaturation of

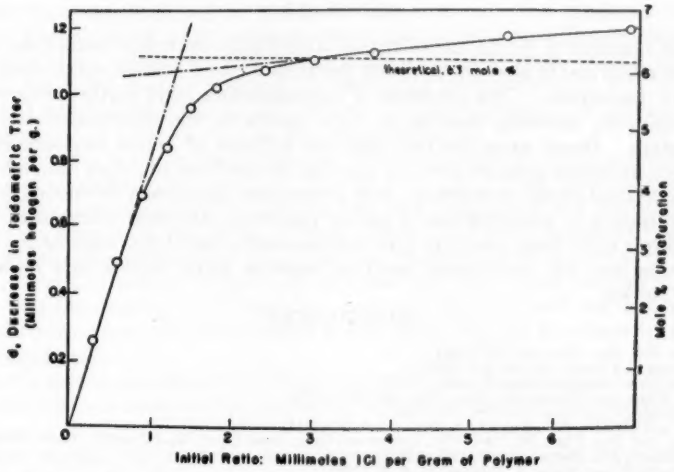


FIG. 10.—Determination of unsaturation of Butadiene butyl rubber by recommended procedure.

butadiene Butyl rubber by the recommended procedure. An unsaturation of 6.0 mole-per cent is found, compared with the "theoretical value" 6.3. The latter value was found by the iodine-mercuric chloride method, which is applicable to butadiene Butyl rubber (to be described in a subsequent publication). The unsaturation of the same sample was found to be 4.1 mole-per cent at the Esso Laboratories by the iodine-mercuric acetate method. However, the Esso value was calculated using an empirical factor of 1.5 molecules of iodine per double bond[4], instead of the theoretical factor 1.0. According to the authors' study of the iodine-mercuric acetate method, the theoretical factor 1.0 should be used for olefins and polymers that are not branched in the immediate neighborhood of the double bond. A recalculation of the Esso value, using the factor 1.0, yields a value of unsaturation of 6.2 in good agreement with the results given above.

As would be expected, and as can be seen from Figure 10, the effect of excess iodine monochloride on apparent unsaturation is much less in the case of butadiene Butyl rubber than in the case of isoprene Butyl rubber. Indeed, a reasonably accurate value of unsaturation of the butadiene Butyl rubber can

be found from a single determination of the decrease in total iodometric titer, provided that the initial ratio of iodine monochloride to double bonds is between 2 and 5 and the reaction period is 1 hour at room temperature.

The recommended procedures described above for determination of unsaturation of highly branched olefins and polymers are not adaptable to routine analyses because they are not rapid. Nevertheless, the procedures are of value in the research laboratory and in the standardization of empirical, routine procedures. A very convenient procedure for determination of unsaturation of isoprene Butyl rubbers is the iodine-mercuric acetate method described by Gallo, Wiese, and Nelson[4]. This method is of much practical importance, although the interpretation of the experimental results involves a numerical factor which at present must be considered empirical.

SUMMARY

The reaction of iodine monochloride with highly branched olefins and polymers is abnormal in that the addition products formed possess steric strain and tend to decompose. The products of decomposition react further with iodine monochloride, generally leading to high results in the determination of unsaturation. Based upon the fact that the addition of iodine monochloride to the decomposition product is not so rapid as the addition of iodine monochloride to the original olefin or polymer, new procedures have been developed for the determination of unsaturation of highly branched ethylenic substances. The procedures have been shown to give reliable results for olefins such as the diisobutylenes and for copolymers, such as isoprene Butyl rubber and butadiene Butyl rubber.

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FAILURES OF RUBBER INSULATION CAUSED BY SOIL MICROÖRGANISMS *

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An earlier paper[1] reported the investigation of the cause of the rare failures of nonleaded rubber-insulated cables buried directly in the ground. These failures were characterized by localized regions of very low insulation resistance. The absorbed water content was no greater than in adjacent regions of high insulation resistance, and the physical properties were usually normal. Drying the failed insulation raised the resistance several decades, but brief exposure to moisture restored the low values. It was suspected that these failures had been caused by the action of soil microörganisms.

A study was made in the laboratory with conditions favoring microbial activity. By exposing thin walls of insulation to soil of high microbe content, adjusted to neutral or slightly alkaline pH, and kept moist and warm, it was possible to accelerate the action so that failures like those occasionally found after ten or more years under actual service conditions were produced in a few weeks. Parallel tests in active soil, sterilized soil, and water showed conclusively that the drastic loss of insulation resistance in active soil was due neither to water absorption nor to the action of soil chemicals, but to attack by living microörganisms.

In the actual operation of underground cables, the most favorable combination of conditions necessary for producing failure by microbial attack occur only rarely.

Since certain soil microbes can consume the natural rubber hydrocarbon, failure of natural rubber insulation is usually accompanied by visible surface pitting. Synthetic-rubber insulation shows no visible signs of attack after even a six decade drop in resistance. This suggests some fundamental difference between the mechanisms of microbial attack on natural-rubber and synthetic-rubber insulation.

The present paper is concerned principally with these mechanisms and with the composition and structure that tend to make rubber insulation vulnerable to such attack. Experimental evidence is given to show that the GR-S and Butyl hydrocarbons are not consumed by soil microörganisms, and that the invisible faults leading to electrical failure occur only where microbes eat out other materials present in the synthetic insulating compound.

METHODS OF LOCATING FAULTS

To study the faults in rubber produced by microörganisms, it is necessary to locate them precisely. Searching along a failed wire sample with a test probe is neither sensitive nor precise enough. Several methods of locating such faults are described below.

* Reprinted from the *Transactions of the American Institute of Electrical Engineers*, Vol. 69, Part II, pages 748–754 (1950). A shortened version of this paper was published in *Electrical Engineering*, Vol. 69, No. 9, pages 782–787, September 1950.

USE OF ELECTROLYTE WITH A COLOR INDICATOR

A simple method of locating faults is to immerse the failed sample in an electrolyte containing phenolphthalein. The conductor is made negative to the bath. Voltages from 100 to 500 volts may be used. At any faults sufficiently leaky the development of alkali produces a red color. Figure 1 shows a failed sample on which 65 color spots could be counted. This method does not mark the faults permanently nor reveal their nature directly.

D-C CORONA TEST

A more sensitive and rapid method is to stress a wet failed wire sample with about 5000 volts (conductor negative) under reduced air pressure. Figure 2 shows a sample with five corona spots. Another sample showed over 20 such spots. The resistance of a single typical fault is of the order of 10 megohms, whereas that of the surrounding intact region is usually of the order of 10,000,000

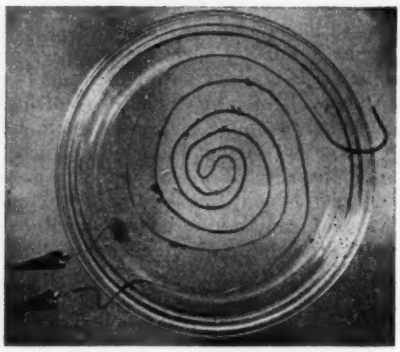

FIG. 1.—Locating faults with color indicator.

megohms per foot of sample. Thus the leaky spots act like point electrodes to produce stress concentrations which break down the air near them. Considerably higher voltage is required to produce corona over-all, so that the effect is clean-cut. Alternating stress would be much less effective because the capacitive current through the whole insulation would mask the leakage current through the faults.

ELECTRODEPOSITION OF COPPER IN FAULTS

Some faults produced by microbes in rubber insulation can be located and permanently marked by immersing failed wire samples in a copper sulfate solution and making the conductor 100 to 500 volts negative to the solution. After a period of several days, surface specks of metallic copper appear at some of the faults. If the treatment is continued these specks grow to copper nodules, while new small specks may appear, as in Figure 3. In a number of samples insulated with laboratory-mixed stock, certain faulty regions showed hundreds of fine copper specks after this treatment, as in Figures 4 and 5.

When the insulation was sliced off to various depths, particles could be found all the way through the wall. These were too minute to be seen by the un-

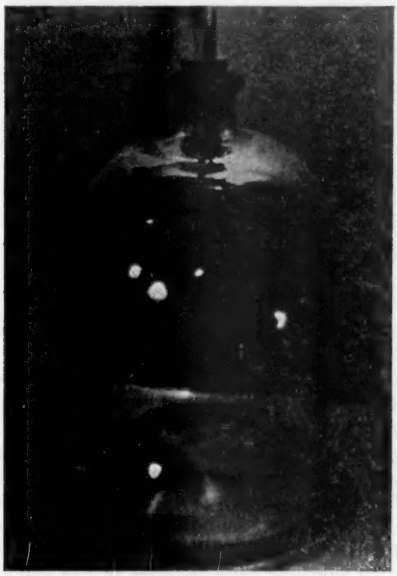

FIG. 2.—Locating faults with d-c corona.

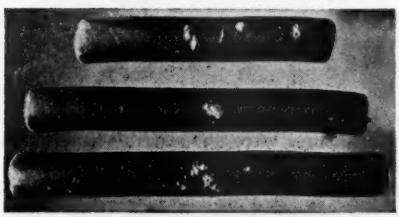

FIG. 3.—Locating faults with electrodeposited copper.

FIG. 4.—Electrodeposited copper showing micropores in natural rubber insulation.

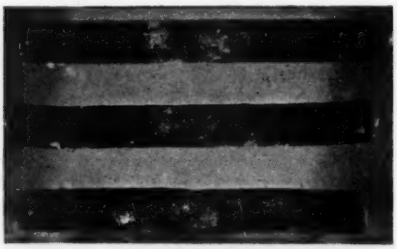

FIG. 5.—Electrodeposited copper showing micropores in GR-S insulation.

aided eye, but their color made them visible at a magnification of 100 ×. To obtain good photographs is was necessary to intensify the specks in the cut layers by additional plating, as in Figure 6.

Of these three methods of locating faults, the electrodeposition of copper on failed samples has shown the most about the nature and distribution of faults. As a quick routine means of counting faults, the d-c corona is more convenient.

Since the first copper ions have to traverse the wall of insulation before they are deposited, the copper filament grows from the conductor outwards. It is extremely fine. After it reaches the surface further deposition leads only to nodule formation, without thickening the filament inside the pore. The copper-bearing channels are not always radial, but sometimes run in many directions, a fact which suggests the existence in the insulation, before microbial attack, of paths more vulnerable than the surrounding insulation.

In the copper-treated faults no continuous, solid filaments have been found that would cause a short circuit. Instead, the pores contained practically single-file aggregates of microscopic copper particles. It was not possible, by dissolving the rubber away, to leave any continuous copper filaments, since they were too fragile.

In the previous paper the presence of invisible faults in GR-S insulations that had failed was demonstrated, but the structure of these faults was not established. Two alternatives were suggested, namely that these faults were either regions of insulation degraded by diffused microbial products until the rubber there had extremely low resistivity or actual holes through the insulation. The results of the copper deposition test show that the faults are holes.

EVOLUTION OF HYDROGEN IN FAULTS

Some failed samples did not show copper specks even though the measured microampere-hours passed through the insulation in the copper sulfate solution were equivalent to an appreciable deposit. If copper were present, but merely too finely distributed to be seen, it could be recovered by electrodeposition on a

FIG. 6.—Section of insulation shown in Figure 4 with copper deposits in micropores intensified by further plating.

platinum wire and weighed. Careful experiments failed to detect any copper in these samples. The leakage current had been carried by ions other than copper ions. Hydrogen ions seemed the most likely carriers. To test this, a sample which had failed to show deposited copper after several days in the copper sulfate bath was placed in the same electrolyte in a glass tube where the hydrogen was collected and measured. After a week a few copper specks appeared, but about 90 per cent of the current through the sample was accounted for by the evolved hydrogen.

Microörganisms could hardly produce a pore with a diameter smaller than that of a copper ion. It is more probable that hydrogen gas evolved at the conductor forms bubbles in the pores that markedly reduce the leakage current. One failed sample showed a four-decade rise in resistance during a prolonged electrolytic test. Soaking in hot water without voltage allowed the hydrogen to diffuse out and restored the initial low resistance.

TWO TYPES OF MICROBIAL ATTACK

When wire samples which have failed in the accelerated laboratory soil exposure test are inspected, the most obvious difference is that the surface of the natural rubber insulation is usually badly pitted, that of the GR-S rubber insulation not at all. This suggests a fundamental difference between the modes of attack on the two types of rubber.

The severe microbial pitting so far found in natural rubber insulation, but not in the synthetics, is the more obvious action, as may be seen in Figure 7.

FIG. 7.—Characteristic pitting of natural rubber.

Its progress can be noted visually long before there is any decrease in insulation resistance. Dielectric strength tests would be expected to show impending failure, but to produce drastic loss of sample resistance the microbes have to eat all the way through to the conductor. The breach in the insulation may eventually become a rather coarse hole rather than a micropore, since there is no reason for the microbes to prefer a radial direction when they can consume the insulation in bulk. It has been shown[3] that a number of soil microörganisms can readily consume natural rubber either as the pure rubber hydrocarbon or as a part of a vulcanized compound. Unless a natural rubber insulation is protected by adequate preventives, the microbes can eventually eat through the wall. This type of attack appears to be little affected by differences in physical texture imparted by variations in processing.

The mechanism of the microbial attack which creates micropores is more obscure. This occurs in both natural and synthetic rubber insulation. In natural rubber the microporous regions are much less numerous than the pitted regions, yet the samples fail through the micropores long before any pits reach the conductor. Figures 4 and 7 illustrate this point. They show two

regions of a sample of natural rubber insulation which had failed in the accelerated laboratory soil test. The electrodeposited copper in Figure 4 shows the presence of many pores that traverse the wall all the way to the conductor. Before the copper treatment this spot showed no visible signs of attack. This was the only microporous region observed. On the other hand, there were very many pitted regions like those show in Figure 7. Although these regions had been exposed to exactly the same conditions, no copper specks were found in these pits nor signs of leakage by any other tests. The wall of insulation under the pits appears to have remained sound. To cause failure by pitting, the microbes have to consume the bulk insulation all the way to the conductor. This is a process which seems to be much slower than the one which creates the micropores.

Figure 6 shows the same microporous region as Figure 4 after 70 percent of the wall had been sliced off and the copper filament ends, visible only under the microscope at 100 ×, had been intensified by additional copper plating.

Since microbial attack on GR-S insulation does not create pits, visual examination does not show whether it has failed or not. Failure is detected by loss of insulation resistance. To locate the faults one of the tests described above is required. Figure 8 shows samples of failed GR-S insulation after copper

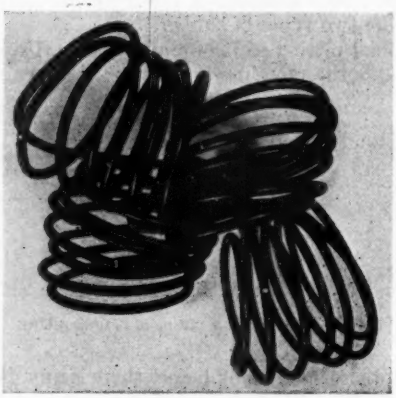

FIG. 8.—Copper deposits on GR-S sample (note absence of erosion).

deposition. Although these samples had suffered a loss of resistance of six decades or more, the surface remained smooth and shiny. The existence of the micropores is revealed by the electrodeposited copper.

In GR-S insulation that failed, the absence of surface erosion, the random direction of the pores, and their minute size imply that the insulation is not uniformly vulnerable, but that even before exposure to soil microörganisms, it contains "imperfections" in otherwise inert material. These are minute veins of microbe food scattered in a random manner throughout a medium that microbes cannot consume. This microbe food is neither water-soluble nor hygroscopic, since control samples in water maintain normal resistance indefinitely. Soil microbes eat out the insoluble food and leave in its place some hygroscopic material. This makes the resistance of the pores very low when the sample is wet, but very high when it has been allowed to dry.

EVIDENCE OF THE EXISTENCE OF IMPERFECTIONS

There is a variety of evidence for the existence of these imperfections. If the bulk insulation could be consumed by soil microörganisms, we should expect, after prolonged soil exposure and failure, to find both severe surface erosion and much larger pores. There would also be no reason for the peculiar orientation and the zigzag course of the pores so often observed when samples are examined after copper deposition. The electrical evidence relating to these imperfections is especially interesting. Considerable light is thrown on the probable structure, both by the trend of insulation resistance versus soil exposure when the test is continued several months after initial failure and by the d-c breakdown values on samples not exposed to soil but simply soaked in hot water.

Figure 9 shows the peculiar trend of resistance of GR-S insulation when exposure to soil is continued after failure. These accelerated laboratory soil exposure tests were made on ten samples of number 14 solid wire with a 3/64- inch wall of a GR-S compound having low water absorption. The samples were consecutive 5-foot lengths from the same length of wire run in the factory. Ten

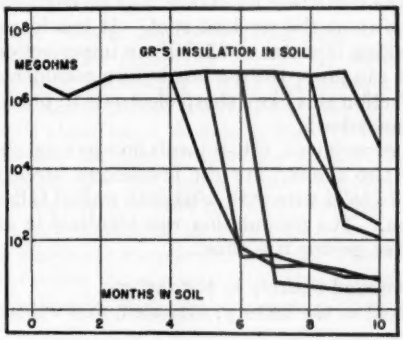

FIG. 9.—Dielectric resistance *vs.* time of exposure to soil.

samples in soil all failed in ten months or less. Four control samples in water maintained normal resistance.

The course of the attack is presumably as follows. Some soil microörganisms, not yet identified, consume food in the minute streaks. Until the first micropore reaches the conductor the effect on the sample resistance is negligible. As soon as the pore passes all the way through the wall, the resistance drops several decades. After this first drop the decrease is very gradual. As more pores traverse the wall they decrease the resistance relatively little. For example, ten faults having equal leakage lower the sample resistance only one decade more than a single fault. If a pore kept increasing in diameter because the microbes could consume the surrounding medium the sample would soon be practically short circuited. This levelling off of the sample resistance after the first sharp decrease, together with the extreme minuteness of the pores and the absence of any visible surface erosion seem to be convincing proof of the correctness of the postulated structure of the imperfections.

There is other independent evidence. Visual tests described later in this paper show that the GR-S hydrocarbon does not support microbe growth, but

that raw GR-S contains materials that do. These materials and others added in the compounding are believed to be the food in the imperfections.

EFFECT OF PROCESSING ON STABILITY OF GR-S INSULATION IN SOIL AND ON D-C BREAKDOWN AFTER HOT WATER SOAK

Whether a given rubber-insulating compound is processed in the factory or in the laboratory, the regular physical and electrical tests usually show no significant difference in quality. In the soil exposure tests, if the insulation is not inherently resistant, or is made so by the addition of effective preventives, wire samples made in the laboratory have almost invariably proved to be more vulnerable than those made in the factory. Thus the structure, as influenced by the processing, that is, the thoroughness and uniformity of mixing, is an important factor in determining the stability in soil.

One of the most effective means of testing rubber insulation for structural imperfections not revealed by low resistance is to make d-c breakdown measurements on samples which have been soaked several days in hot water. If fissures, micropores, or poorly bonded interfaces extend only partly through the wall their effect on the insulation resistance may be negligible. Direct voltage stress causes breakdown at the weakest spot. It is a local, not a bulk effect. After a few days soaking in water at 158° F, an imperfection in only a fraction of the wall thickness can lower the d-c breakdown considerably. Water which diffuses to an imperfection acts like a sharp electrode to produce high local stress concentration and breakdown.

In the following experiment, GR-S insulation having abnormal vulnerability to soil microbes also showed low d-c breakdown strength. Samples were prepared of number 14 solid wire with 3/64-inch wall of GR-S insulation having low water absorption. The formulation was identical in all samples, but the processing in the three groups was thus:

1. Insulation processed entirely in the factory.
2. Insulation mixed in the factory, extruded, and vulcanized in the laboratory.
3. Insulation processed entirely in the laboratory.

The usual tests for insulation resistance *vs.* soil exposure were made on samples from each group. Table I shows the initial megohms and the megohms after four months in soil (five feet buried length). Another set of samples from the same groups was soaked three days in water at 158 degrees Fahrenheit and then broken down by d-c stress.

Control samples for the soil tests showed no drop in insulation resistance in water. Samples from each group, after being dried two days at 185° F, showed an average value of 2300 volts per mil, apparently not significantly affected by the variations in processing. Thus the major physical factor affecting both stability in soil and d-c breakdown strength is the completeness of mixing. Although the low d-c breakdown voltages and the rapid failure in soil may not both be caused by the same imperfections, it is evident that the kind of mixing that produces the highest d-c breakdown after hot soak also increased the stability in active soil. It is not surprising that the factory mixing should prove superior.

The difference with regard to stability in soil is one of degree only. The results in Figure 9 and those in the third column of Table I were obtained with samples from the same length of factory-run wire. The better mixing thus

TABLE I

EFFECT OF PROCESSING ON STABILITY AND BREAKDOWN

Laboratory mixed and insulated	Factory mixed laboratory insulated	Factory mixed and insulated
Initial megohms in soil		
2,700,000	2,100,000	2,500,000
2,700,000	2,200,000	3,000,000
2,700,000	2,300,000	3,100,000
2,900,000	2,200,000	3,500,000
Megohms after 4 months in soil		
400	3,300,000	2,000,000
6	2,900,000	2,100,000
3	3,100,000	2,300,000
4	700	2,400,000
Volts per mil d-c breakdown after 3 days in water at 158° F		
750	1000	1100
750	1200	1200
700	1100	1300
700	1200	1200

merely delayed failure. These were only 5-foot lengths, yet in one sample the d-c corona test revealed 20 micropore faults. It seems unlikely that any amount of mere physical processing would guarantee unlimited stability in service lengths of thousands of feet, which a few microbe faults might put out of operation. On the other hand, certain types of GR-S insulation made inherently resistant by the addition of effective microbe preventives have been stable in soil even when the processing is not thorough enough to produce optimum d-c breakdown strength after hot water soaking. The d-c breakdown strength after hot water soaking is thus an index of structural integrity, regardless of inherent resistance to microbe growth. The visual fungus test described later shows whether the material is inherently resistant to microbe attack without regard to the thoroughness of mixing. These two tests are entirely independent.

The ideal insulation is one combining maximum resistance to microbe growth with the best possible physical structure.

PROTECTION OF INSULATION BY JACKETS— STAGGERED IMPERFECTIONS

Tough Neoprene jackets are commonly used over the insulation of nonleaded underground cables to provide mechanical protection and weather resistance. It is desirable that they should also protect the insulation against attack by soil microörganisms. It is not satisfactory to test the resistance of Neoprene jacket compounds to microbial attack by extruding them directly on a copper conductor and measuring insulation resistance *vs.* soil exposure. The resistivity of such compounds is inherently low, and this tends to mask the effect of failures produced by microörganisms.

The most significant laboratory test is carried out by coating wire with insulation known to be susceptible to microbes, applying a layer of Neoprene compound over this, burying the samples in soil, and making periodic megohm measurements between conductor and soil. The resistance of the jacket is so low that it does not interfere with the measurement.

Since two different mechanisms of attack had been observed in the failures of natural rubber and GR-S insulation, it was of interest to test the effect of

Neoprene jackets over both types. Ten five-foot samples of number 14 solid wire with 3/64-inch wall of a natural-rubber insulation and a 25-mil wall of Neoprene jacket compound were buried in soil, and four were immersed in water. Those in water showed normal high resistance during 13 months. All ten soil test-samples failed in 9 to 13 months, with an average drop in insulation resistance of three decades. This is less than that observed when the insulation is directly exposed to soil. Even an imperfect jacket delays the attack and restricts it to a small fraction of the total area. These failures indicate that the microbes traverse the Neoprene jacket, presumably through food streaks or imperfections. When they reach the natural rubber at any point they can cause failure by consuming the bulk insulation.

In a parallel test ten samples with similar jackets but with GR-S insulation showed no decrease in resistance during 15 months in soil. Four control samples in water also maintained normal resistance. Two samples of the same GR-S insulation without jackets showed normal resistance for ten months, but drops of four to six decades after 13 months.

The marked difference in relative stability of the GR-S and the natural rubber insulation under Neoprene jackets of identical type is most easily explained by applying the imperfection theory to the case of two layers. Since microbes cannot consume the bulk material of either Neoprene or GR-S, they have to find imperfections in both to cause failure. Even when these are numerous, the probability of an imperfection in the jacket registering exactly with one in the insulation is small. If this does happen, the sample should eventually fail. In general, the imperfections would be expected to be staggered in such a way that failures in jacketed GR-S samples would be rare.

In another experiment to test this idea, a 2-layer GR-S insulation is being compared for stability in soil with a single layer of the same thickness.

The statement in the earlier paper that Neoprene compounds appear to be inherently resistant to soil exposure is true only in the sense that like GR-S, they do not show visible results of microbe attack. If a Neoprene jacket contains food streaks, microbes can eat through it and attack susceptible natural rubber under it.

In a preliminary experiment samples of wire insulated with a 15-mil wall of vulcanized latex covered with a 20-mil wall of a Neoprene jacket compound were exposed to soil until they had failed. The jacket was stripped from short pieces, and these were quickly placed on sterile nutrient agar. In a few days white colonies starting from the wire spread gradually over the agar surface. The microörganism was identified as a species of Fusarium.

Experiments of this type are valuable both to show that microbes can traverse the jacket and also to identify those that do.

ACCELERATED VISUAL TEST OF MICROBIAL ATTACK

The decisive laboratory test of the stability of underground cable insulation is the periodic measurement of insulation resistance of samples buried in soil for long periods under conditions most favorable to microbial attack. In this test susceptible samples fail in a few months. As compounds more resistant to soil exposure are developed, the time to failure may become excessively long. A means of quickly showing whether a compound is inherently resistant to soil microbes is of great advantage.

A simple visual test provides such a means. Small pieces of material, which may be either vulcanized insulation or raw rubber or other polymer, are placed

on a thin layer of soil sprinkled over moist sand. The test may be accelerated by dusting the sample lightly with dried soil. The amount of material for such a test is very small and much processing time is saved.

Most susceptible materials show considerable fungus growth in a week or two. For example, the GR-S insulation on the samples of Figure 9, some of which took ten months to fail electrically, showed profuse fungus growth in about two weeks on the visual test. This test shows whether the insulating compound is inherently resistant and is independent of the degree of mixing.

FIG. 10.—Visual fungus test on raw GR-S with additives.

One use of this visual test is illustrated in Figure 10. The samples are pieces of raw GR-S 65 with various additives. At the left is a blank containing no additives. All samples had equal milling. Figure 11 shows an unmilled lump of GR-S after several weeks in a closed bottle over inoculated water. Without other tests the profuse growth of fungus on the raw GR-S could be misleading.

FIG. 11.—Fungus on raw GR-S.

When the same type of GR-S has been acetone-extracted, it shows no fungus growth after many months on this test. Even if the GR-S is badly oxidized after extraction by prolonged heating, it does not support growth. The GR-S hydrocarbon is not a source of microbe food. When the acetone extract is evaporated on aluminum foil and exposed to soil, heavy fungus growth appears, as is evident in Figure 12. The immunity of purified GR-S supports the im-

FIG. 12.—Fungus on acetone extract of raw GR-S.

perfection theory of failure of GR-S insulation. It accounts for the absence of surface erosion.

Growth of fungus on a particular insulation in the visual test does not prove that failure in soil of that insulation was directly caused by fungus. The fungus serves as an indicator which shows whether the compound is attractive to microorganisms in general. In doubtful cases the visual test may not be a sufficient criterion. On the other hand, an insulation that supports profuse fungus growth would be a poor risk for underground cable insulation. A large number of unpromising materials can be screened out with little effort. To date the routine soil exposure tests on rubber insulation have confirmed the predictions of the visual test.

A practical application of this test is illustrated in Figures 13 and 14. Both samples have similar GR-S insulation of low water absorption, but with differ-

FIG. 13.—Visual fungus test on GR-S compound A.

ent combinations and amounts of preventives. Compound A showed visible fungus growth in one week. Compound B showed no growth during nine months test. Thus the implication of the visual test was that compound A would be unstable in soil, B stable.

To check this, 5-foot lengths of number 14 solid wire with 3/46-inch wall of insulation were prepared. Four samples of each type were buried in active soil, four in sterilized soil, and four immersed in water. In water and in sterilized soil all samples maintained normal resistance for a year. In active soil all four samples of compound A, which showed fungus in the visual test in one week, failed after three to five months. The four samples insulated with compound B, which showed no growth on the visual test, maintained normal high resistance for one year. These results confirmed the predictions of the visual test for these particular compounds.

A similar confirmation was obtained with the natural-rubber samples jacketed with a particular Neoprene compound. The jacket showed profuse fungus growth on the visual test. The corresponding ten samples failed in the accelerated soil exposure test.

FIG. 14.—Visual fungus test on GR-S compound B.

Visual fungus tests on individual materials aid in the choice of compounding ingredients. It is not safe, however, to use these results to predict the stability of complete insulating compounds. For example, although raw Neoprene, both as received and after extraction with alcohol, shows no fungus growth in this test, a typical Neoprene jacket compound may support profuse growth within a week. Certain insulating compounds may show no growth in the unvulcanized condition, but abundant fungus after vulcanization. The interaction of compounding ingredients during vulcanization may change susceptibility to microörganisms. The only safe test is one made on the final insulation. If a compound shows no appreciable fungus growth, the visual test should be followed up by making periodic measurements of insulation resistance on wire samples buried in soil.

Pure natural-rubber hydrocarbon supports the growth of microörganisms. In the visual test the first growth seems to be Actinomycetes, which appear

wherever the sample contacts the soil. This is followed by fungus growth. Raw Butyl rubber generally shows little or no fungus growth. A slight growth of an organism cultured and identified as a species of Tricoderma was observed on some samples, but acetone-extracted Butyl rubber shows no growth at all. Butyl rubber severely oxidized after acetone extraction also fails to show growth of fungus. Paraffin wax and Heliozone show excessive growth. A high paraffin content tends generally to make compounds more susceptible to microbial attack. In Neoprene compounds the effect of paraffin is peculiar. It blooms rapidly to the surface where it supports heavy fungus growth. A number of preventives that are effective in insulating compounds do not inhibit such growth on Neoprene compounds, presumably because they are not sufficiently soluble in the paraffin layer. They also may reach the surface more slowly than the paraffin. If the microörganisms merely ate off the paraffin film without further action, this would not be cause for concern. It is not safe to rest on that assumption. This is shown by the failure of the samples jacketed with Neoprene compounds that showed fungus growth in the visual test.

SUMMARY

The failure of rubber insulation brought about by soil microörganisms can best be detected by a decrease of several decades in the insulation resistance. To study the mechanism of attack and the physical structure that makes rubber insulation vulnerable to such attack, it is necessary to have means of locating and marking the failed spots. Several methods of doing this have been described. The electrodeposition of copper in the micropores created by microbes affords the best insight into the physical structure of the faults. Two distinct modes of attack have been shown. The simpler one, which is characteristic of natural rubber, is a progressive eating away of the bulk insulation. The second, a more obscure type, creates micropores through the wall, but without visible surface erosion. This mode is typical of the synthetics, in which the base hydrocarbon or polymer, if freed of extraneous microbe food, does not support microbe growth. The imperfections consist of streaks of microbe food scattered in a random manner through otherwise inert material. Their distribution is affected by physical processing. These streaks are not hygroscopic and do not lead to failure in prolonged immersion in either hot or cold water. They do, however, tend to lower the d-c breakdown of samples after several days soaking in hot water. Thus with a given susceptible compound it is possible to predict which processing will produce the greatest stability in soil by breakdown tests on samples not exposed to soil. The breakdown tests relate to physical structure. To test the inherent resistance of a material to soil exposure, the simple visual fungus test is very convenient. The validity of this test as a criterion of stability has so far been confirmed by the routine resistance tests after accelerated laboratory soil exposure. It is not safe to predict the stability of a complete compound from the results of visual tests on the base material. The vulcanized insulation must be tested. Insulating compounds shown to be promising by the visual test should be given a thorough soil exposure test.

The testing of preventives is a field in itself. It is not simple. Materials which are strongly antiseptic in water may not be so when mixed in a rubber compound. Many of them would be completely unsuitable in rubber insulation. Some preventives are effective in a compound before it is vulcanized but not afterwards. Some are completely inactivated by certain other necessary

or desirable ingredients. Others may leach out in time and cease to protect the material. Oxidation inactivates some preventives. A nicely balanced compound is required to produce insulation with sufficient stability in soil, proper physical characteristics, and high electrical quality.

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CHLORINATION OF NATURAL RUBBER. I. PREPARATION AND PROPERTIES OF CHLORINATED RUBBER *

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INTRODUCTION

The chlorination of rubber has been the subject of extensive investigations[1], the rubber being commonly treated in solution with gaseous chlorine at a given temperature and pressure. The properties of the products of rubber thus treated vary in close dependence on the chlorine content, which may be as much as 70 per cent. The drawback to a low chlorine content is that, as a rule, the chlorine is loosely bound, with the result that, when exposed to heat or light, it splits off as HCl, with formation of discolored and cyclized products and serious deterioration of the mechanical properties. But the higher the chlorine content, the more stable are these chlorinated rubbers. The stability of chlorinated products of natural rubber containing approximately 65 per cent of chlorine is such that they are used commercially as a component of anticorrosive paint.

The instability of chlorinated rubber of low chlorine content is closely connected with its chemical constitution and the mechanism of reaction. The current opinion ten years ago[2] was that chlorine first adds to the double bond of the rubber, and that this primary product, while splitting off HCl, enters into further reaction with chlorine; but reexamination of this reaction in the laboratory of our affiliated English organization[3] and independently in our own laboratory has led to very different views. It was realized that rubber dichloride (the addition product of chlorine and rubber) is far too stable to act as an unstable intermediate product during the chlorinating reaction. Bloomfield[4] argued that, during the primary reaction, the chlorine is attached by substitution to an α-methylenic carbon atom of the rubber molecule and that there is a considerable amount of cyclization.

It was not our sole concern to study the mechanism of reaction; we were also bent on following the chlorination of rubber under the most diverse conditions, starting from dry rubber, rubber in solution, and rubber in latex, and with highly diversified sources of chlorine such as from liquid chlorine, gaseous chlorine, hypochlorites, and sulfuryl chloride.

The normal course of reaction, involving the formation of unstable intermediate products, is discussed in Part I of this series; methods of producing comparatively stable rubber chlorides by adding chlorine onto the double bond are considered in Part II.

THE ANILINE TEST

The reaction of halides with organic bases has been used in this laboratory for the kinetic identification of halide groups in polymers[5]. It is sufficient for

* Reprinted from the *Journal of Polymer Science*, Vol. 6, No. 6, December 1950; Part I from pages 639–651; Part II from pages 653–665. These papers are Communications No. 114 and No. 115 of the Rubber Foundation, Delft.

the purpose of this and the subsequent papers to state that allylic chlorides and tertiary chlorides react with aniline at 100° C in a very short time, while dichlorides with vicinal chlorine and polychlorides of the chlorinated rubber type split off only part of the chlorine and at much lower rates. Certain polychlorides with the $>CCl_2$ group are, however, unstable at 100° C in aniline, and this can interfere with the kinetic separation. The reactivity of typical mono- and dichlorides is summarized in the left-hand part of Figure 1; the analogous reaction of some polymers with a polychloride structure is given in the right-hand half.

A polymer or a mixture of polymers consisting of allylic and (or) tertiary groups react very fast until all the reactive chlorine has been split off. This, in fact, is observed in the chlorination products of rubber (see Figure 2).

Polymers with 30–55 per cent total chlorine content split off part of their chlorine very fast, while the "slow" fraction reacts frequently with a rate found for chlorinated rubber with 64 per cent Cl (curve 4, Figure 1). The exact amount of reactive chlorine can be determined by an extrapolation to time zero.

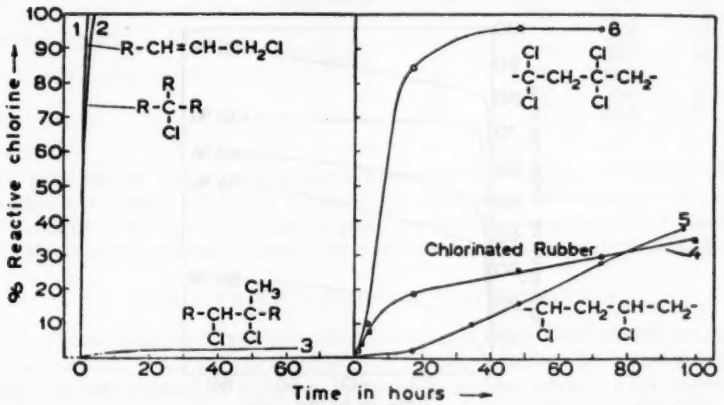


FIG. 1.—Reactivity of chlorides with aniline at 100° C. *Model Compounds:* 1, allylic chlorides; 2, tertiary chlorides; 3, vicinal dichlorides. *Polymers:* 4, chlorinated rubber with about 64 per cent chlorine; 5, polyvinyl chloride; 6, polyvinylidene chloride.

Above a total chlorine content of 55 per cent, this reactivity with aniline becomes less significant for two reasons: (1) the bend in the reaction time curve becomes less pronounced and extrapolation to time zero therefore becomes uncertain; and (2) $-CCl_2$ groups may be present and can interfere with the determination of the allylic fraction.

The reactivity with aniline by itself does not prove that the reactive fraction is allylic. Additional kinetic experiments[6] would be necessary to distinguish between allylic and tertiary chlorine in cases where it is not obvious from the type of reaction (chlorination or hydrochlorination, respectively).

Experiments were performed by heating 0.1–0.2 gram of polymer with 4 cc. of purified aniline in a sealed tube. The contents of the tube were rinsed in a beaker with dilute (1:1) nitric acid and silver nitrate added. The dyestuffs formed from aniline were removed with charcoal and the filtered solution was titrated according to Volhard.

As a matter of convenience we have usually determined the amount of re-

action of chlorinated rubber with aniline after a heating time of 17 hours at 100° C. It is clear from Figure 2 that this value may be 4 to 7 per cent higher than the extrapolated value, an inaccuracy which does not influence our conclusions.

CHLORINE GAS WITH RUBBER IN SOLUTION

With the object of discovering the optimum conditions for the production of chlorinated rubbers of greater stability than usual, a large number of experiments were carried out in which rubber in solution was made to react with gaseous chlorine. These experiments, which are recorded in Tables I and II, were carried out quite simply by introducing gaseous chlorine into roughly 100 cc. of a rubber solution stirred vigorously. In some cases a solution of gaseous chlorine in carbon tetrachloride was added dropwise instead of introducing gaseous chlorine as such. The natural rubber used was masticated standard sheet or crepe; the deproteinized rubber a commerical crepe grade; the gutta-percha specially purified by recrystallization of first quality commercial gutta-percha. The reaction product was reprecipitated for analysis by dissolving it

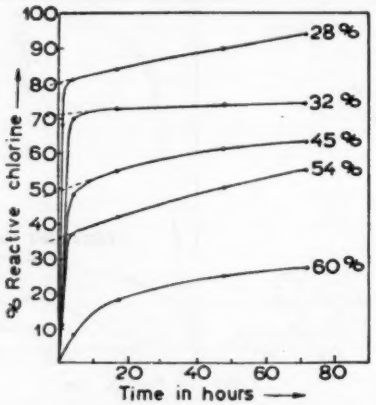


FIG. 2.—Reaction of chlorinated rubber with aniline at 100° C. The figures on the curves refer to the total chlorine content of the polymer.

in benzene or chloroform and precipitating with alcohol. The Carius method was employed to determine the chlorine content. Generally, these determinations were accurate within 0.5 per cent.

The nature of the reaction products is characterized by the percentage of reactive chlorine, *i.e.*, the portion of combined chlorine which is reactive in the aniline test (17 hours 100° C). It is found that the stability of the products toward aniline is quite independent of the experimental conditions. Although the percentages of reactive chlorine vary strongly, the responsible factor has been found on careful investigation to be the total chlorine content of the reaction product. This chlorine content of chlorinated rubbers is governed by the duration and intensity of chlorination. A somewhat larger chlorine content is usually obtained at higher temperatures, *e.g.*, 50 to 70° C, than at 0 to 20° C. The addition of benzoyl peroxide (Bz_2O_2) as a catalyst does not affect the nature of the chlorine and certainly does not help to increase the chlorine content. Experiments with purified gutta-percha have proved that exhaus-

TABLE I

CHLORINATION OF NATURAL RUBBER AND GUTTA-PERCHA IN 5 PER CENT SOLUTION WITH CHLORINE GAS

Polymer	Solvent	Catalyst	Time (hours)	Temp. (° C)	% Cl in product	% reactive Cl of total
Natural rubber	$CHCl_3$	—	17	−70	41.5	55
Deproteinized rubber	CCl_4	—	1	5	43.5	70
		—	2	5	49.5	65
		—	4	5	62.0	30
		—	7	5	64.0	15
		O_2	2	5	50.5	58
		O_2	7	5	50.5	57
Natural rubber	CCl_4	—	1	20	36.5	79
		2% Bz_2O_2	1	20	27.0	80
		—	2	20	48.0	57
		—	7	20	62.5	17
Gutta-percha	CCl_4	—	0.5	20	22.5	75
		5% Bz_2O_2	0.5	20	22.0	74
		—	1.5	20	58.5	19
Natural rubber	CCl_4	—	1	77	49.0	37
		5% Bz_2O_2	1	77	35.0	63
		—	4	77	60.5	13
		—	8	77	65.5	14
		—	16	77	68.0	21

tive purification of the polyisoprene hydrocarbon also has no visible effect. Oxygen has a slight inhibiting effect during continued chlorination. Exposure to the light of an ordinary tungsten lamp hardly influences the rate of reaction, but ultraviolet light has a considerable influence, as is evident from Table II.

SOME EXPERIMENTS ON FRACTIONATION

Products of about 30 per cent chlorine content, when fractionated, are found to be nonhomogeneous. A more regular reaction appears to result from the dropwise introduction of chlorine dissolved in carbon tetrachloride instead of in the gaseous form, but it is clear from the following experiments that even then the products are nonhomogeneous.

1. At −10° C, 10 grams chlorine, dissolved in 86 cc. CCl_4, were added drop by drop to 20 grams masticated crepe dissolved in 400 cc. CCl_4, the material being stirred constantly. The resulting product contained 18.5 per cent of chlorine. This product was fractionated by solution in $CHCl_3$ (3 per cent

TABLE II

INFLUENCE OF LIGHT ON CHLORINATION WITH GASEOUS CHLORINE OF NATURAL RUBBER IN 5 PER CENT CCl_4 SOLUTION (REACTION TIME, 7 HOURS)

	Dark		100-watt electric bulb		U.V. light quartz	
Temp. (° C)	% Cl in product	% reactive Cl	% Cl in product	% reactive Cl	% Cl in product	% reactive Cl
0	59.0	40	62.0	17		
20	62.5	19	64.0	17		
50	60.5	30	64.0	17	66.5	18
77	65.0	16	65.0	18	70.0	57

solution) and precipitating with progressive amounts of isoamyl alcohol. The following were obtained:

42% of a fraction with 41.3% Cl
7% of a fraction with 35.0% Cl
38% of a fraction with 1.5% Cl
13% of a fraction with 0.5% Cl

2. Another chlorinated rubber, treated in the same way, contained 18.0 per cent of chlorine. This was fractionated by dissolving in benzene and precipitating in fractions with acetone and then with ethyl alcohol. The following were obtained:

37% of a fraction with 1.1% Cl
27% of a fraction with 22.5% Cl
36% of a fraction with 30.5% Cl

The chlorine in the two latter fractions was found to be reactive in the aniline test to the extent of 90 to 95 per cent, which means that the fractions contain approximately that amount of allylic chlorine.

A few experiments were also performed in a film reactor, but with the same result, *viz.*, the formation of nonhomogeneous products. We shall see in Part II of this series that it is possible to obtain homogeneous products by chlorinating with SO_2Cl_2.

The extremely rapid reaction between rubber and chlorine is in all probability responsible for this nonhomogeneity. This reaction, betrayed by the evolution of HCl, is seen to occur as soon as gaseous chlorine or a chlorine solution is mixed with the rubber solution, and it is a tenable conjecture that the conversion takes place in a matter of a fraction of a second. Then, the viscosity of the solution stands in the way of rapid intensive mixing, with the result that, even with intensive stirring, there are likely to be local high concentrations of chlorine, in the vicinity of which the rubber reacts with greater ease than elsewhere in the solution.

CHLORINATION UNDER PRESSURE

There was good reason to believe that if the pressure of the chlorine gas was raised, the reaction of chlorine with rubber would be accelerated and the chlorine content of the chlorinated rubber increased. A special device was made by which rubber in solution can be chlorinated under pressure—see Figure 3.

The apparatus comprises a couple of bronze autoclaves. A glass jacket in an autoclave of 200 cc. capacity contains about 100 cc. of a rubber solution. It is necessary to have chlorine gas flowing continuously through the solution to keep the latter sufficiently saturated and homogeneous, and also to evacuate the HCl formed during the reaction. An exhaust is accordingly provided for the surplus gas *via* a condenser through a regulated pressure valve. The required chlorine is in the liquid state in the other autoclave connected by pressure pipe with the reaction autoclave. The autoclaves can be heated to any temperature required. By keeping the temperature of the chlorine autoclave 10 to 20° C below that of the reaction autoclave, a constant stream of chlorine gas can be made to bubble through the solution *via* a silver inlet tube.

It was found expedient to chlorinate the rubber solution in the ordinary way for some time before applying pressure. The impression from a comparison of Table III with Table I is that the application of pressure certainly does produce

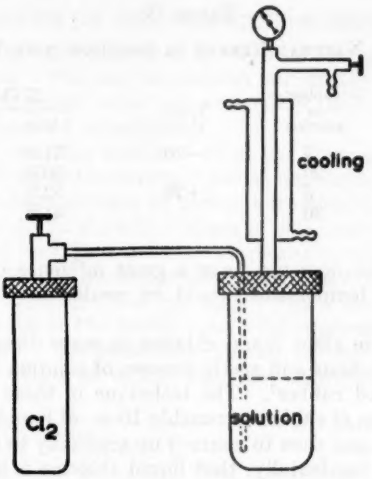


FIG. 3.—Apparatus for chlorinating rubber solutions under pressure.

a higher chlorine content in less time. An added advantage is that the material can thus be chlorinated at temperatures far above the boiling point of the solvent. On the evidence of the recorded intrinsic viscosities, the solubility of the resulting products is satisfactory. Without exposure to light it is exceedingly difficult to obtain chlorine contents above 65 per cent at ordinary pressure, so large-scale production of chlorinated rubber of a high chlorine content would without doubt benefit by the application of pressure.

CHLORINATION WITH LIQUID CHLORINE

The next point on our program was to discover how rubber responds to chlorination with liquid instead of gaseous chlorine. We can see from Table IV what happens when liquid chlorine reacts at relatively low temperature with rubber in solution. In these experiments 10 cc. liquid chlorine was mixed with 10 cc. solution at −70° C and, if necessary, was then warmed up in a closed tube to the desired reaction temperature. Apparently, the reaction, in the main, occurs at −70° C. The chlorine content does not differ appreciably from that resulting from chlorination with gaseous chlorine, which proves that the

TABLE III

INFLUENCE OF PRESSURE ON CHLORINATION OF NATURAL RUBBER IN 3 PER CENT CCl_4 SOLUTION

First phase: chlorination at atmospheric pressure for 4 hours at 45° C

Pressure, atm.	Second phase temp. (° C)	Time (hours)	Per cent Cl in product	$[\eta]^a$
7	70	5	65.5	0.48
11	70	2	67.5	0.18
12	120	2	66.5	0.14
13	90	2	68.5	0.09

[a] Intrinsic viscosity of the polymer solution in $CHCl_3$, determined at 25° C in an Ostwald viscometer.

TABLE IV

CHLORINATION OF NATURAL RUBBER IN SOLUTION WITH LIQUID CHLORINE

Solvent	% rubber in solution	Temp. (° C)	% Cl in product	
			1 hour	17 hours
$CHCl_3$	5	−70	51.0	54.5
	20		50.0	54.0
CCl_4	5	+20	52.5	58.5
	20		51.0	56.0

chlorine concentration does not have a great influence on the course of the reaction. A higher temperature would be needed to obtain larger chlorine content.

It was tempting to allow liquid chlorine to react direct with solid rubber, thus obviating the tedious and costly process of solution involved in the production of chlorinated rubber[7]. The technique in these experiments was to add about half a gram of rubber to roughly 10 cc. of liquid chlorine at −70° C in a small autoclave, and then to warm it up gradually to the desired temperature. It was found incidentally, that liquid chlorine is an excellent swelling agent for rubber. When the reaction has ceased, the chlorine is evaporated and the resulting chlorinated rubber purified by dissolving it in $CHCl_3$ and precipitating with alcohol.

It will be seen from the data of Table V that the reaction proceeds with greater velocity at higher temperatures, when the normal chlorine contents for commercial chlorinated rubber are obtained and surpassed. There is, however, one serious drawback to this method: if the rubber and liquid chlorine are warmed too quickly, the reaction is likely to be too violent and to cause charring. There may even be signs of kindling when finely divided pieces of rubber or gutta-percha are introduced into liquid chlorine at −50° C. It is, therefore, necessary to be on guard against any reaction of chlorine with rubber in anything like large quantities, and one should, in any case, beware of letting liquid chlorine react at the more elevated temperatures with major amounts of rubber all at once, as the reaction is likely to become uncontrollable[8]. The products are generally insoluble, only those containing a very large percentage of chlorine (65–70 per cent) being soluble. Apparently, cross-linking reactions are apt to occur during chlorination as a secondary reaction, but this is a much rarer occurrence with chlorination in dilute solution because the solvent molecules keep the rubber molecules further apart. The solubility of products of large chlorine content is due to chlorinolysis. Under the severe conditions employed, the chlorine disrupts C—C bonds of the chlorinated rubber molecules with the formation of smaller fragments.

TABLE V

CHLORINATION OF SOLID NATURAL RUBBER WITH LIQUID CHLORINE

Temp. (° C)	Time (hours)	% Cl in product	% reactive Cl
−70	17	38–43	50–40
−40	17	49–57	50–20
20	3–60	50–60	40–20
50	5	60	20
70	3–6	63–64	14–25
100	3–6	68–70	30–41
120	1–3	68–69	35

CHARACTER OF THE CHLORINE–RUBBER BOND

Some experiments were performed to discover how much chlorine is combined by substitution. This can be deduced fairly easily from the quantity of hydrochloric acid generated, since one molecule of HCl is liberated for every chlorine atom combined by substitution.

In these experiments, the results of which are given in Figure 4, a solution of chlorine gas in carbon tetrachloride of known concentration was dripped into a given amount of rubber solution in carbon tetrachloride at 60° C. It would seem that it is especially in the initial stages of chlorination (below 30 per cent of combined chlorine) that the reaction proceeds almost entirely by substitution. In the case of products with 50–55 per cent of combined chlorine, the chlorine is bound additively to the extent of 40 per cent. This is consistent with the view that addition of chlorine on the double bond follows substitution of one chlorine atom per isoprene unit. The possibility remains, however, that there may be a certain amount of splitting-off of HCl from the chlorinated rubber during the

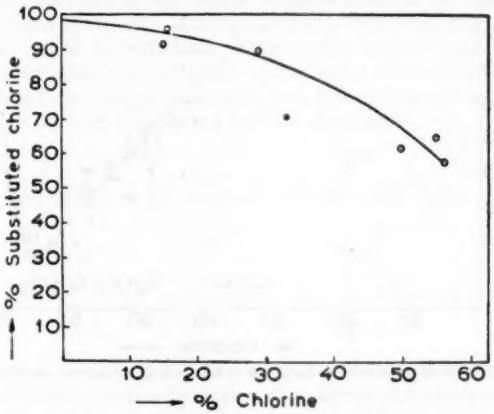


FIG. 4.—The quantity of substituted chlorine as a function of the chlorine content.

reaction. The aniline test indicates that the primarily bound substitution chlorine possesses a reactivity which, according to experiments with model substances, fits in with a linkage at the allylic position.

It will be seen from Figure 5 that the quantity of reactive chlorine split off in the aniline test decreases with increasing chlorine content. Products containing about 30 per cent of chlorine show that roughly 80 per cent of this chlorine is reactive in the aniline test. This reactivity drops to approximately 15 per cent in chlorinated rubbers with 60–66 per cent, but begins to increase again above 67 per cent of chlorine.

The remarkable point about this is that the results recorded in Figure 5 are those obtained with chlorinated rubbers produced under the most divergent reaction conditions with variation of temperature, pressure, source of chlorine (gaseous or liquid), rubber (solid or in solution), exposure to light, and catalysts. It is evident, therefore, that however much we varied these conditions, we were unable to combine chlorine with rubber in any fundamentally different way. The minor variations found in Figure 5 may be due in part to lack of homogeneity of the chlorinated rubber. In Part II we shall discuss methods that do make

it possible to combine chlorine with rubber in a different way and to which the relation found in Figure 5 does not apply.

The results of the aniline test tend to show that in all instances the chlorine is first mainly bound by substitution at an allylic position. With 50 per cent of chlorine, chlorinated rubber contains, on an average, two chlorine atoms per isoprene unit. We have to assume that roughly half the isoprene units contain only one loosely bound allylic chlorine atom, whereas the other half of the isoprene units contain three atoms far more firmly attached. This is compatible with an average reactivity of the total chlorine in a chlorinated rubber of this kind with aniline of approximately 45 per cent. The increase in reactivity with aniline of chlorinated rubber containing more than 67 per cent of chlorine may be due to the formation of $—CCl_2$ groups, which are very reactive with aniline, as has been shown in Figure 1 for polyvinylidene chloride.

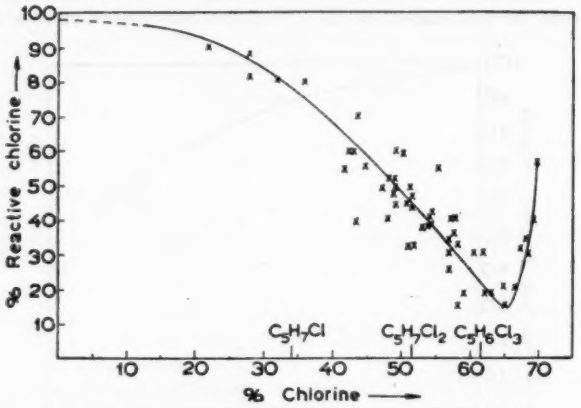


FIG. 5.—Percentage of reactive chlorine in the aniline test as a function of chlorine content.

It has been stated[9] that a substitution of chlorine at the allylic position is likely to occur at very low temperatures (0 to −60° C), with great rate of reaction in the chlorination of branched olefins, such as isobutene and trimethyl ethylene, in the liquid phase. The following two chlorides are formed from trimethyl ethylene:

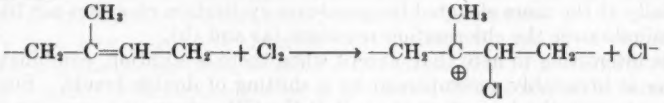
$$CH_3—\underset{\displaystyle CH_3}{\overset{|}{C}}=CH—CH_3 + Cl_2 \longrightarrow$$

$$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}—CHCl—CH_3 \quad \text{and} \quad CH_2Cl—\underset{\displaystyle CH_3}{\overset{|}{C}}=CH—CH_3 + HCl$$

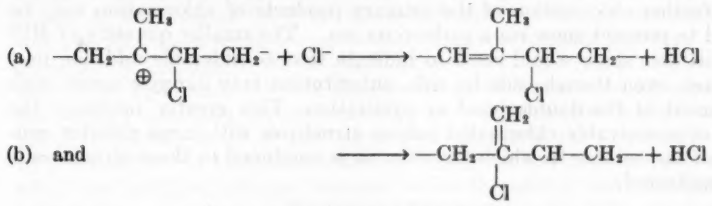
when at the same time allylic rearrangement between the two products takes place. This substitutive chlorination of isobutylene and trimethyl ethylene illustrates a fairly general rule formulated by Kondakoff[10] in 1891 to the effect that olefins which combine readily with mineral acids yield monochloroolefins, whereas those which do not, yield the normal addition products on treatment with chlorine. Natural rubber and gutta-percha possess a structure very similar to that of trimethylethylene, and these polymers combine readily with a

mineral acid such as HCl. Thus the primary substitutive reaction of these polymers is in line with the behavior of olefins in general.

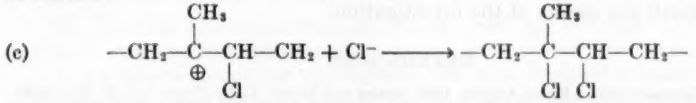
Although the chlorination of hydrocarbons generally constitutes a free radical type of reaction, it is nevertheless a tenable conjecture that, with olefins, the primary reaction in chlorination is of an ionic nature[11]. It has been found that the normal primary chlorination of rubber and like olefins with chlorine cannot be accelerated by normal free-radical chain-initiating agents. Nor can the chlorination be arrested by the known chain reaction inhibitors. Arguments can be advanced[12] to show that the rate-determining step is addition of a positive chlorine ion to the double bond to form a carbonium ion and a negative chlorine ion.



The intermediate carbonium ion follows several distinct reaction courses. It may be that a proton splits off. The double bond resulting from the elimination of the proton is formed preferentially between the carbon bearing the positive charge and that adjacent carbon atom which is the most richly endowed with electrons, and it is from this carbon atom that the proton splits off[12]. We may then obtain the following chlorinated rubber structures:

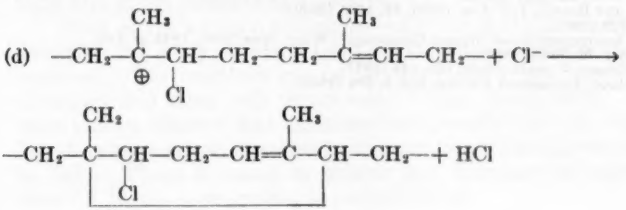


Apart from this, we have to allow for the possibility of the carbonium ion's reacting with a Cl^- ion with the formation of a normal chlorine addition product, as follows:



On the evidence of the quantity of HCl split off and the results of the aniline test, however, it is quite certain that only infinitesimal amounts of this rubber dichloride are formed, if at all.

Bloomfield[4] argues from iodine number determinations that the following cyclization reaction is likely to take place:



In view of the fact that chlorinated rubbers in solution are of relatively low viscosity compared to their molecular weight, Staudinger and Staudinger[13] likewise come to the conclusion that considerable cyclization must have taken place during the chlorination. These authors assign a different structure to cyclized chlorinated rubber from that suggested by Bloomfield. They presume that the methyl group reacts with the main chain during cyclization, and that other unknown cyclization reactions also occur. It is certainly not difficult to see that there are alternatives to the structure assigned by Bloomfield to cyclized chlorinated rubber. The fact alone that the reaction products of liquid chlorine with solid rubber are usually insoluble shows that not only intramolecular, but also intermolecular cross-linking reactions are probably involved. Especially at the more elevated temperatures cyclization reactions are likely to predominate over the chlorination reactions (a) and (b).

It is interesting to note that, except when there is addition, combination of chlorine is invariably accompanied by a shifting of double bonds. Such displacement, with the formation of an $R_1R_2C{=}CH_2$ group, is borne out by the evidence of infrared investigations[15].

When chlorination is slow, we must be prepared to find that the HCl evolved may be added on to the original polyisoprene double bond. This side reaction, which leads to rubber hydrochloride structures, can be avoided by chlorinating quickly, or by immediately evacuating the HCl generated by means of an inert gas.

The further chlorination of the primary products of chlorination may be supposed to proceed anew *via* a carbonium ion. The smaller quantity of HCl evolved at this stage would seem to indicate that considerable addition now takes place, even though, side by side, substitution may likewise occur, with displacement of the double bond or cyclization. This greatly increases the number of conceivable chlorinated rubber structures with large chlorine contents, and the manner in which the chlorine is combined in these structures is very complicated.

ACKNOWLEDGMENT

The authors wish to express their thanks to W. H. Manger and J. V. van Ulden for their valuable assistance, and to the Rubber Foundation for permission to publish the results of the investigation.

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II. PREPARATION AND PROPERTIES OF RUBBER DICHLORIDE

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INTRODUCTION

As we have seen in Part I, the chlorination of rubber with chlorine under the most varied conditions leads to products in which the chlorine is initially attached fairly loosely to an allylic carbon atom[1]. Consequently, chlorinated rubbers of low chlorine content have rather poor properties.

We shall now proceed to describe two methods by means of which, with saturation of the double bond, chlorine is introduced into rubber and the formation of products with allylic chlorine is avoided. In this way chlorinated rubbers of comparatively low chlorine content can be obtained, and these are considerably more stable than the products of the same chlorine content resulting from the direct chlorination of rubber. One of these methods depends on a catalytic additive chlorination of rubber with sulfuryl chloride; the principle of the other is the addition of HCl onto rubber followed by normal chlorination.

The aniline test described in Part I (in which the chlorinated rubber is heated with aniline for 17 hours to 100° C) was again employed to establish the nature of the chlorine bond in chlorinated rubber. Under the conditions of this test, allylic and tertiary combined chlorine reacts quantitatively. Chlorine attached by addition to the double bond of the rubber reacts to the extent of only about 4 per cent. We are therefore in a position to mark off clearly allylic and tertiary chlorine from addition chlorine. This reactive tertiary chlorine is introduced into rubber by the addition of HCl, with the formation of rubber hydrochloride. In the chlorination of rubber we are mainly concerned with allylic and addition chlorine, between which the aniline test distinguishes unmistakably. Moreover, the splitting off of the chlorine from chlorinated rubber with aniline gives us a good idea of its chemical stability.

REACTION OF SO_2Cl_2 WITH ORGANIC SUBSTANCES

SO_2Cl_2 is an interesting reagent because there are different ways in which it reacts with organic substances[2].

It is a source of chlorine molecules at the more elevated temperatures or in presence of halogen carriers, such as iodine. Under these conditions the same chlorinating reaction can be induced as with gaseous chlorine, with the advantage that the reaction is far more orderly with SO_2Cl_2. This form of reaction has already been applied to natural rubber[3].

The second kind of reaction results in the introduction of a sulfonyl chloride group into organic molecules and takes place at 40–60° C under exposure to light and in the presence of a catalyst, *e.g.*, pyridine[4].

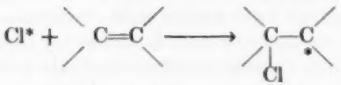
There is yet another technique—effecting a chain reaction catalyzed with peroxide, the study of which has been the special concern of Kharasch and coworkers[5]. The reactions can be divided roughly into two classes, those with saturated and those with unsaturated organic compounds. Various substitutions can be effected with saturated compounds[6] and the results are more or less the same as those obtained by chlorination with chlorine gas under exposure to light. There is reason to believe that this reaction proceeds *via* chlorine atoms. It has been applied to polyethylene[7].

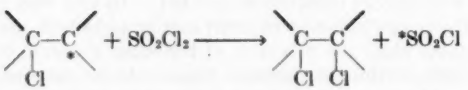
The chain reaction of SO_2Cl_2 with ethylenic compounds is of particular interest to those concerned with rubber[8]. Substances such as cyclohexene, allyl chloride, and the like react with SO_2Cl_2 when the corresponding dichlorides are formed; hence, the double bond becomes saturated as chlorine is added on. Catalysts such as ascaridole or benzoyl peroxide are used. Kharasch and Brown[9] drew up the following scheme for a chain reaction of this kind:

$$\text{Peroxide} \longrightarrow R^*$$

$$R^* + SO_2Cl_2 \longrightarrow RCl + {}^*SO_2Cl$$

$${}^*SO_2Cl \longrightarrow SO_2 + Cl^*$$





REACTION OF SO_2Cl_2 WITH GUTTA-PERCHA

Bloomfield[10] has applied the free-radical chain reaction of SO_2Cl_2 to rubber. He found that peroxides such as benzoyl peroxide catalyze the additive chlorination of very carefully purified natural rubber. With ordinary crepe rubber, on the other hand, the reaction was for the most part substitutive. It would seem that the contaminations of nonpurified rubber interfere with the free-radical chain reaction.

For a reliable study of the reaction between SO_2Cl_2 and natural rubber, therefore, a necessary condition is that the rubber used should have previously been dependably freed from all nonrubber constituents. Exhaustive purification of natural rubber, however, is a very difficult and tedious process. Here, Nature comes to our aid, for gutta-percha is a natural *trans*-isomer of polyisoprene, with chemical properties very similar to those of natural rubber, and it is very easily purified. There is good reason to believe that those reaction conditions that are found to apply to gutta-percha are valid for natural rubber.

Commercial gutta-percha of prime quality is purified by dissolving it in petroleum ether at an elevated temperature and then crystallizing the gutta-percha by cooling the solution down to 0° C, when the crystal mass can be filtered off and dried. The melting point of purified gutta-percha is approximately 65° C.

The results of some reactions of SO_2Cl_2 with gutta-percha solutions in carbon tetrachloride of a 3 per cent concentration by weight are listed in Table I. In these and subsequent experiments the quantity of solution was generally 60 cc., to which SO_2Cl_2 was added in the amount calculated to produce a chlorine content of 25 to 35 per cent. The recorded times of reaction can generally be considerably shortened if peroxides are present, in which case the whole reaction is completed within a very short period (in about five minutes) with the evolution of a great deal of heat. Table I shows that chlorine combines during the reaction of purified gutta-percha with SO_2Cl_2. The combined chlorine has very little reactivity in the aniline test. The addition of peroxides, or radiation with ultraviolet light, produces virtually the same results. The slight reactivity of the chlorine in the aniline test goes to show that there has been addition of

TABLE I

REACTION OF SO_2Cl_2 WITH GUTTA-PERCHA IN A 3 PER CENT CCl_4 SOLUTION

Conditions	Time (min.)	Temp. (° C)	% Cl in product	% reactive Cl
As such	30	20	24.0	7
As such	10	5	32.5	6
+ ultraviolet light	30	20	34.5	5
+5% tetralin hydroperoxide	30	20	30.5	6
+5% benzoyl peroxide	2	10	32.5	6
+5% benzoyl peroxide	10	20	28.5	7
+5% benzoyl peroxide	30	77	37.5	7

chlorine, a fact which was, moreover, proved by measurements made of the quantity of HCl which would have been evolved during a substitutive reaction. Very little HCl, or none at all, was formed during the experiments recorded in Table I. The additive chlorination reaction of SO_2Cl_2 with gutta-percha is entirely comparable to the additive reactions found by Kharasch and Brown[9] with olefins under the catalytic influence of peroxides. The very fact that an additive reaction is found with gutta-percha in itself points to the presence of gutta peroxides.

The particulars given in Table II corroborate the supposition that the reaction with gutta-percha is actuated by a chain mechanism. It is evident from Table II that certain antioxidants serve as inhibitors in the additive chlorination reaction with gutta-percha. Insofar as there can be said to be any reaction at all, this, on the evidence of the percentage of reactive chlorine, takes place mainly by substitution. The substitutive reaction is fostered by letting the reaction take place at higher temperature, because this facilitates the decomposition of SO_2Cl_2 and the formation of chlorine molecules[11] which react in the ordinary way, that is to say, substitutively. The more soluble the agents are, so much more effectively do they inhibit the reaction. Hydroquinone dissolves badly and is, therefore, less useful than di-*tert*-amylhydroquinone or β-naphthol. The very fact that substances exist which completely inhibit the additive reaction proves that there is a chain reaction. This chain reaction is obviously initiated by peroxides; hence the inhibitive effect of the antioxidants mentioned consists either in neutralizing the peroxides or reacting with whatever radicals are liberated from those peroxides.

An entirely different state of affairs is revealed by Table III, from which it is clear that numerous substances, including several antioxidants, not only inhibit the additive reaction, but so change the course of things that, judging by the percentage of reactive chlorine, a considerable substitution of chlorine takes place. A fact common to all the catalysts listed in Table III is that they

TABLE II

REACTION OF SO_2Cl_2 WITH GUTTA-PERCHA IN A 3 PER CENT CCl_4 SOLUTION IN THE PRESENCE OF INHIBITORS

Inhibitor	Time (min.)	Temp. (° C)	% Cl in product	% reactive Cl
5% hydroquinone	60	20	8.5	64
5% hydroquinone	90	20	10.0	77
5% di-*tert*-amylhydroquinone	90	15	6.5	91
5% β-naphthol	90	20	4.5	73
5% β-naphthol	60	70	21.0	72

contain nitrogen in the form of amino or nitroso groups. The substances probably owe their effect to their ability to liberate molecular chlorine from SO_2Cl_2 or to act as chlorine transmitters, when the chlorine reacts exactly as does ordinary chlorine gas, that is to say, substitutively. The quantity of HCl evolved was a further attestation to the presumed substitution of chlorine. The fact that only 80 per cent of the combined chlorine is reactive would seem to show that some of the chlorine is not held at the allylic position, or that certain changes of structure have taken place during chlorination, possibly owing to cyclization and displacement of the double bond.

REACTION OF SO_2Cl_2 WITH NATURAL RUBBER

The reaction of SO_2Cl_2 with rubber in solution was initially studied for the main purpose of producing homogeneous products containing from 20 to 50 per cent of chlorine. We saw in Part I that it is a fairly simple matter to obtain products of this chlorine content by introducing chlorine gas into a rubber solution, but that, on fractionation, these products vary enormously in chlorine content. SO_2Cl_2, however, provides a means of obtaining products that are homogeneous[12]. The required quantity of SO_2Cl_2 was mixed with the rubber solution at a low enough temperature, *e.g.*, 0°C, to ensure homogeneous mixing

TABLE III

REACTION OF SO_2Cl_2 WITH GUTTA-PERCHA IN A 3 PER CENT CCl_4 SOLUTION IN THE PRESENCE OF CATALYSTS

Catalyst	Time (min.)	Temp. (° C)	% Cl in product	% reactive Cl
5% aldol-α-naphthylamine	60	20	27.0	79
5% phenyl-β-naphthylamine	60	20	27.0	81
5% pyridine	60	20	22.5	82
5% diazoaminobenzene	12	20	23.5	81
5% diazoaminobenzene	60	20	28.5	81
Some NO gas	60	20	30.5	80
5% cetylpyridinium bromide	60	20	28.5	74
5% tetraphenylhydrazine	15	30	23.0	80
5% isoamyl nitrite	30	20	30.0	79

before the reaction started. The reaction can be set in motion after the materials have been mixed, either by waiting for some time, or by raising the temperature slightly.

Table IV shows that the reaction with sheet or deproteinized crepe is substitutive, which is comprehensible, since sheet contains roughly 7 per cent of nonrubber components, consisting partly of amino acids and amines. These nitrogen-containing substances have the same catalytic effect on the reaction as the agents listed in Table III. The deproteinized crepe is a commercial product which still contains 1 to 2 per cent of nonrubber components, which apparently is quite enough to deflect the reaction toward substitution. The results are improved by careful purification of the rubber by treating latex with caustic soda and then extracting the rubber, but this is a very tedious process. Fractionating tests proved that the reaction products are, on the whole, highly homogeneous.

We see from Table V that ultraviolet irradiation of the reaction mixture in a quartz tube favors additive reaction. The low percentage of reactive chlorine testifies to the fact that ordinary and deproteinized rubber yield an addition

TABLE IV

REACTION OF SO_2Cl_2 WITH NATURAL RUBBER IN A 3 PER CENT CCl_4 SOLUTION

Rubber	Time (min.)	Temp. (° C)	% Cl in product	% reactive Cl
Standard sheet	20	0	29.5	96
	60	20	20.0	86
	60	20	38.0	75
	60	77	28.5	88
	60	77	47.5	49
Deproteinized crepe	60	25	24.0	87
	60	77	29.0	82
Deproteinized purified rubber	30	25	31.0	19
	30	25	28.5	31

product in the main, especially at low temperature. The other auxiliaries used, with the exception of ascaridol, have no appreciable effect. The startling point about this is the virtual inertia of benzoyl peroxide, which used to be a favorite promoter of the additive reaction. The probable explanation is that the quantity of radicals formed out of benzoyl peroxide is too small to suppress the substitutive reaction accelerated by the natural amines present.

It is evident from Table VI that organic hydroperoxides are exceedingly active chain initiators of the additive chlorination of rubber. These substances are apparently able to defeat the substitutive catalysis of the nonrubber components. The procedure is to add the hydroperoxide and subsequently the SO_2Cl_2 to the rubber solution. After a short induction time, the reaction starts violently, with the evolution of a great deal of heat. As a rule, the reaction is completed within three minutes, though the mixture is generally allowed to continue to react a little longer, as in the majority of the experiments to which Table IV refers. It is advisable to mix at low temperature, *e.g.*, 0° C, so that the reaction shall not begin before the SO_2Cl_2 has properly mixed with the ma-

TABLE V

REACTION OF SO_2Cl_2 WITH NATURAL RUBBER IN A 3 PER CENT CCl_4 SOLUTION IN THE PRESENCE OF CHAIN INITIATING AGENTS

Rubber	Catalyst	Time (min.)	Temp. (° C)	% Cl in product	% reactive Cl
Sheet	2% benzoyl peroxide	60	20	25.0	86
	5% benzoyl peroxide	60	77	27.5	82
Crepe	5% urea peroxide	40	20	6.5	81
	5% di-*tert*-butyl peroxide	40	20	11.5	75
	3% *tert*-butyl perbenzoate	40	20	13.5	76
Deproteinized crepe	5% ascaridol	60	25	29.5	17
	5% ascaridol	60	77	26.0	68
	5% benzoyl peroxide	60	20	19.0	77
	Ultraviolet light	60	4	17.0	21
	Ultraviolet light	30	20	28.0	8
	Ultraviolet light	30	77	27.5	43
Crepe	Ultraviolet light	60	0	20.5	28
	Ultraviolet light	60	15	27.5	17
	Ultraviolet light	60	20	22.5	49
	Ultraviolet light	60	40	25.5	70
	Ultraviolet light	60	77	26.5	83

terial. At the higher temperatures, *e.g.*, 77° C, the reaction is less favorable for addition, possibly because the peroxide then decomposes too soon and because SO_2Cl_2 dissociates more readily at high temperature into chlorine molecules[11] which react substitutively. It has been found that more than 3 per cent of hydroperoxide relative to the rubber is required if the additive reaction is to proceed satisfactorily. The chlorine content of the end products depends on the quantity of SO_2Cl_2 used. Generally speaking, a yield of 80 to 90 per cent of the SO_2Cl_2 may be depended on for additive reactions in presence of hydroperoxide. As a rule, the products also contain 1 to 2 per cent of combined sulfur, which may be present in the form of SO_2Cl_2 groups or as added on SO_2 evolved in the course of the reaction. The theoretical chlorine content of 51 per cent is never attained. Then, some degree of substitution sometimes occurs and the chain reaction can come to a standstill if the reaction proceeds too

TABLE VI

REACTION OF SO_2Cl_2 WITH NATURAL RUBBER IN A 3 PER CENT SOLUTION IN THE PRESENCE OF HYDROPEROXIDE CHAIN INITIATORS

Rubber	Solvent	Catalyst*	Time (min.)	Temp. (° C)	% Cl in product	% reactive Cl
Sheet	CCl_4	5% ethyl HP	60	25	26.0	13
	CCl_4	5% ethyl HP	30	77	17.5	60
Deproteinized crepe	CCl_4	5% ethyl HP	60	77	16.5	33
Crepe	CCl_4	5% tetralin HP	10	25	23.5	6
	CCl_4	5% tetralin HP	60	25	35.0	5
	$CHCl_3$	5% tetralin HP	30	20	24.5	36
	Benzene	5% tetralin HP	30	20	26.0	11
	CCl_4	1% *tert*-isobutyl HP	30	20	10.5	23
	CCl_4	3% *tert*-isobutyl HP	30	20	27.5	5
	CCl_4	4% *tert*-isobutyl HP	30	30	47.0	7
	CCl_4	4% *tert*-isobutyl HP	30	40	43.5	14
	CCl_4	5% *tert*-isobutyl HP	30	20	28.0	5
	CCl_4	5% 1-hydroxy-cyclohexyl HP	30	15	20.0	7

* HP = hydroperoxide.

slowly. The best reactions with the best yields are those which are obtained in the shortest time.

ANALYSIS OF SOME OF THE REACTIONS

(1) 5.02 grams SO_2Cl_2 was added to 100 grams of 3.06 per cent solution of crepe in carbon tetrachloride. These reacted first 45 minutes at 25° C, then 45 minutes at 75° C. The escaping reaction gases—which may consist of SO_2, HCl, and some unconsumed SO_2Cl_2—were collected in NaOH solution, in which chloride content was determined by titration, the SO_2 content by iodometry, and the SO_4 content (derived from SO_2Cl_2) by gravimetry. According to the SO_2 Collected, 4.2 grams of SO_2Cl_2 had reacted. The amount of HCl collected was 1.232 grams, 0.270 gram of which was derived from distilled SO_2Cl_2. From this we are able to calculate that 3.56 grams of SO_2Cl_2 had reacted

substitutively and, therefore, 0.64 gram additively. Hence the chlorine content of the chlorinated rubber should be 29.4 per cent, 74 per cent of which was substituted. Actually the product contains 28.9 per cent of chlorine, 83 per cent of which is found to be reactive according to the aniline test.

(2) 153 mg. (5 per cent) tetralin hydroperoxide and 4.24 grams SO_2Cl_2 were added to 100 grams of a 3.06 per cent solution of crepe in carbon tetrachloride, these reacting for 30 minutes at 25° C, and then for 30 minutes at 75° C. On the evidence of the SO_2 collected, 2.62 grams SO_2Cl_2 had reacted with the rubber. 0.16 gram HCl was collected, this being derived entirely from distilled SO_2Cl_2. From these data the calculated chlorine content of the chlorinated rubber is 31.5 per cent, added on to the extent of 100 per cent. In fact, the product contains 29.7 per cent chlorine, 8 per cent of which is reactive according to the aniline test. The product also contains 1.3 per cent sulfur.

Both these experiments, which could be supplemented by others, demonstrate the reliability of the aniline test as a standard for the degree of substitution and addition, since the results of this test accord with the quantity of HCl collected and the amount of SO_2Cl_2 which had reacted.

GELATION OF ADDITIVE CHLORINATED SOLUTIONS

One danger attending the preparation of additive chlorinated rubber with SO_2Cl_2 is that after the reaction the solution may show a strong tendency to jellify. Some experiments were performed with the special intention of discovering the conditions which encourage this gelation and how it is to be avoided. The line mainly followed was to observe the changing viscosity, determining this by approximation by measuring the time of efflux from a pipet. The following conclusions were drawn.

(1) The rate of gelation depends on the reaction temperature. A higher temperature, though the contrary of conductive to additive chlorination, causes less gelation in the solution of the reaction product.

(2) The rate of gelation increases with the gelation temperature. A given reaction mixture jellifies at 65° C within two hours of the reaction, within five hours at 20° C, and within 72 hours at 0° C. During the reaction itself, which is often accompanied by elevation of temperature, considerable increase in viscosity takes place as compared to that of the initial solution.

(3) Light appreciably fosters gelation.

(4) Traces of water, *e.g.*, 1 per cent relative to the solution, considerably accelerate gelation, even in the dark. Antioxidants, such as benzidine or di-*tert*-amylhydroquinone, have no effect at all.

(5) The gases NO or N_2O_3, introduced in small amounts into the reaction mixture, arrest gelation both in darkness and in light.

(6) The addition of a small amount of HI solution to the reaction mixture not only prevents any increase in viscosity, but even reduces it substantially in the long run. In a given instance the viscosity was reduced by half after three hours at 0° C and after 72 hours at 20° C to as much as one-tenth, thus dropping to the viscosity of the initial rubber solution. Iodine too, which is always present in HI, similarly decreases the viscosity. The smallest amount still producing perceptible effect was 0.6 per cent HI + 0.1 per cent I_2 (relative to the chlorinated rubber) in a 10 per cent solution in H_2O. The reducing effect on the viscosity increases with the amount of HI used.

(7) A small amount of chlorine gas first increases the viscosity, this being

followed by rapid and effective decrease on exposure to diffuse daylight. HCl has no effect.

(8) The addition of approximately 5 per cent of a hydroperoxide (relative to the chlorinated rubber) to the solution after the reaction stops gelation and greatly reduces the viscosity.

We thus see that there are various means by which gelation can be counteracted. The cause of gelation is not yet properly understood, but it may be suggested that the free radicals still present after the reaction initiate cross-linking reactions between the chlorinated rubber molecules. If this is so, the effect of HI, for example, would be due to destruction of the free radicals present. Similarly, the breaking up of the polymer network would be responsible for the activity of a hydroperoxide or chlorine and light.

Some connection might be suggested with the gelation which occurs during the reaction of SO_2 with rubber under the influence of a peroxide, with the formation of rubber sulfones[13], as SO_2 in large quantities is also liberated in the reaction of SO_2Cl_2 with rubber in the presence of the same peroxides as those employed for the SO_2–rubber reaction.

CHLORINATION OF RUBBER HYDROCHLORIDE

The chlorination of rubber in solution leads to partially cyclized chlorinated rubber derivatives, in which the chlorine is distributed rather at random in the

TABLE VII

CHLORINATION OF RUBBER HYDROCHLORIDE IN A 2.5 PER CENT CCl_4 SOLUTION WITH CHLORINE GAS

Conditions of light	Time (hrs.)	Temp. (° C)	% Cl in product
Darkness	3	25	35.5
Darkness	3	77	44.0
Daylight	3	25	60.0
Daylight	3	77	59.0
Electric 100-watt light	3	20	62.0
Ultraviolet light	3	20	71.5
Ultraviolet light	3	77	69.5

molecule. Rubber hydrochloride, in which the double bonds are saturated by the addition of HCl seemed a suitable starting material for the production of more precisely defined chlorinated rubber derivatives. It is probable, moreover, that owing to the absence of double bonds only linear, noncyclized molecules of chlorinated rubber are formed.

The chlorine content of the rubber hydrochloride used was 30.1 per cent and it was prepared by dissolving commercial Pliofilm in chloroform and precipitating with alcohol. As a rule 60 cc. of carbon tetrachloride solution in a concentration of 2.5 per cent by weight were used for an experiment. Table VII shows that radiation with light, especially with ultraviolet light, greatly accelerates the reaction[14], which tends to result in chlorinated rubbers of exceptionally high chlorine contents, comparable with those obtained by direct chlorination of rubber[1]. There were several substances which had an inhibiting effect on the chlorination at room temperature in daylight, *viz.*, diazoaminobenzene, phenyl β-naphthylamine, and tetralin peroxide, in particular. Some degree of inhibition was experienced with oxygen too, which is consistent with its well-

known inhibitive effect on the chlorination of paraffins[15]. Iodine, on the other hand, in amounts as much as 5 per cent relative to the rubber hydrochloride acted catalytically even in darkness, thus promoting chlorination.

As is evident from Figure 1, the percentage of reactive chlorine, as determined by the aniline test, was found to stand in a striking relation to the chlorine content in chlorination experiments carried out at room temperature. The introduction of a new chlorine atom into rubber hydrochloride stabilizes the chlorine atom already produced by the hydrochlorination. The total amount of the chlorine in rubber hydrochloride is reactive in the aniline test proving that this chlorine is attached to the tertiary carbon atom. By the introduction of a second chlorine atom, which is fully accomplished with a Cl content of

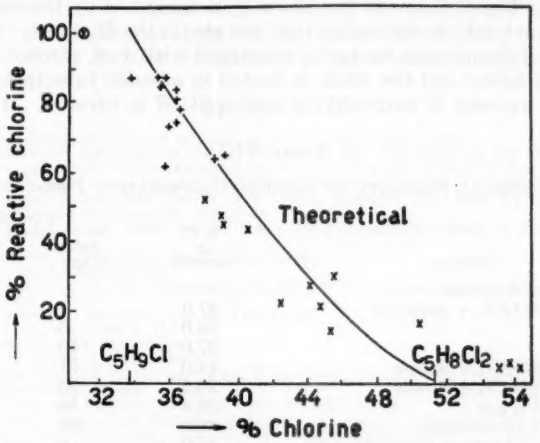
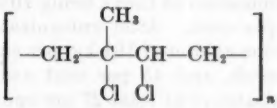


FIG. 1.—Relation between chlorine content and percentage of reactive chlorine of chlorinated rubber hydrochloride.

51 per cent, a product is obtained in which both chlorine atoms are stable according to the aniline test. Figure 1 shows the theoretical line calculated on the assumption that every chlorine atom introduced stabilizes a chlorine atom already present. The experimental data approximate this line very closely.

In monochloroparaffins, substitution of a second chlorine atom is often directly adjacent to the first[16]. It is also a general rule that secondary carbon atoms are chlorinated more quickly than primary ones[17]. If this is assumed also to hold good for the chlorination of rubber hydrochloride, the structure of a chlorinated rubber hydrochloride with 51 per cent Cl should be mainly as follows:



This is the same structure as that of the product obtained from the reaction of SO_2Cl_2 with rubber under the influence of a peroxide. The two products do, in fact, exhibit the same stability toward aniline, whereas the product derived

from the direct chlorination of rubber containing 51 per cent of chlorine is reactive to the extent of 45 per cent.

Quite probably, however, the second chlorine atom is not always substituted on the same side as the first one, in which case the structure may be less regular than suggested. There is undoubtedly some substitution of chlorine at the primary carbon atom (in the methyl group). Substitution of chlorine at the following secondary carbon atom (in the 1,3-position) cannot be ruled out completely, but it is unlikely because the tertiary chlorine atom would then be more reactive in the aniline test than it has in fact been found to be.

STABILITY AND MECHANICAL PROPERTIES

The chemical stability of various products of chlorination is evident from Table VIII. The evidence of this stability is furnished by the splitting off of the chlorine, not only in the aniline test, but also in the H_2O test. In the latter test 1 gram of chlorinated rubber is moistened with 1 cc. alcohol, after which 25 cc. H_2O is added and the whole is heated in a sealed tube to 100° C for 17 hours. The amount of hydrochloric acid split off is titrated. The recorded

TABLE VIII

CHEMICAL STABILITY OF VARIOUS CHLORINATION PRODUCTS

Polymer	% Cl in product	% reactive Cl	
		Aniline test	H_2O test
Chlorinated rubber			
With SO_2Cl_2 + peroxide	47.0	4	0.8
	38.0	5	1.2
	27.0	10	0.3
With SO_2Cl_2 + amine	44.0	71	2.5
With SO_2Cl_2 + amine	29.5	90	7.3
With Cl_2 gas	50.5	58	1.6
Rubber hydrochloride	30.0	100	27
Chlorinated rubber hydrochloride	53.0	6	0.2

percentages of split off chlorine are relative to the total amount of chlorine originally present. It is clear from Table VIII that the aniline and H_2O tests produce correlating figures. The stability of the products of the addition of Cl_2 to rubber with SO_2Cl_2 and peroxide, and that of chlorinated rubber hydrochloride is considerably greater than the stability of the others.

The mechanical properties of products chlorinated by addition depend very much on the chlorine content. A product of additive chlorination containing 23.5 per cent chlorine (prepared with SO_2Cl_2) was vulcanized for 10 minutes at 110° C, the composition being 100 parts of rubber, 1 part of zinc oxide, 2 parts of sulfur, 1 part of zinc diethyldithiocarbamate, 5 parts of triethylamine, 2 parts of the antioxidant Nonox. The tensile strength of this vulcanizate was 120 kg. per sq. cm., the elongation at break being 705 per cent. Its swelling in hexane amounted to 150 per cent. After vulcanization, a rubber of this kind with 27.0 per cent of chlorine exhibited 181 kg. per sq. cm. tensile strength, 365 per cent elongation at break, and 45 per cent swelling in hexane. Hence, chlorinated rubber vulcanizates of at least 27 per cent chlorine content may be said to belong to the category of nonswelling rubbers. The recovery after elongation of these rubbers, however, is very slow and they are difficult to vulcanize. Their insufficient stability is an obstacle to their vulcanization at temperatures in the neighborhood of 145° C.

Products of higher chlorine content come into the thermoplastic class of materials. A product containing 38.0 per cent chlorine and compounded in the proportion of 100 parts of chlorinated rubber to three parts of magnesium oxide was pressed at 100° C to a small sheet having 480 kg. per sq. cm. tensile strength, 850 kg. per sq. cm. flexural strength, and 29 cm. kg. per sq. cm. impact resistance.

One drawback to chlorinated rubber of a chlorine content below 50 per cent for use as a plastic is the comparatively low softening point, which is about 90° C. Chlorinated rubber hydrochloride with 42 to 52 per cent chlorine is known to possess good film-forming properties[18].

ACKNOWLEDGMENT

The authors wish to express their thanks to W. H. Manger and J. V. van Ulden for their valuable assistance, to Dr. G. Salomon for his interest and suggestions, and to the Rubber Foundation for permission to publish the results of the investigation.

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KINETIC ANALYSIS OF ORGANIC HALIDES. II. ANALYSIS OF MACROMOLECULES BUILT UP OF MONOHALIDE UNITS *

G. SALOMON AND C. KONINGSBERGER

INTRODUCTION

A kinetic method of analysis for the identification and kinetic separation of organic monohalides with the aid of organic bases, has been described[1]. In this paper we shall apply this new method to the analysis of polymers. Many polymers containing halogen are known, but in most of the familiar ones, like polyvinyl chlorides and polyvinylidene chlorides (the polymer of 1,1-dichloroethylene), halogen atoms are separated by only one CH_2 group, and the polymer is, therefore, derived from a low molecular polyhalide, *e.g.*, —CHCl——CH_2—CHCl—, rather than from a monohalide. A large group of polymers can be prepared by addition of HCl or HBr to polymeric olefins, which belong frequently to the class of natural or synthetic rubbers; in this case only one halogen atom is carried by a group of at least four carbon atoms. Such polymers may be assumed to correspond in their reactivity to low-molecular monohalides. Another group belonging to the same class are the polymers of chloroprene and similar halogenated butadienes.

The homogeneity of halogen structure in the polymer and the identity of this group with model compounds can be tested by kinetic analysis. A discrepancy in the reactivity of the polymer and that of a model compound does not immediately prove a difference in structure, but may be due also to physical factors, such as a slow rate of diffusion into the polymer. We shall deal essentially in this paper with the first problem, and treat the physical phenomena only as a possible source of experimental errors. It should, however, be kept in mind that the halide-amine reaction may be used for the study of diffusion phenomena in polymers.

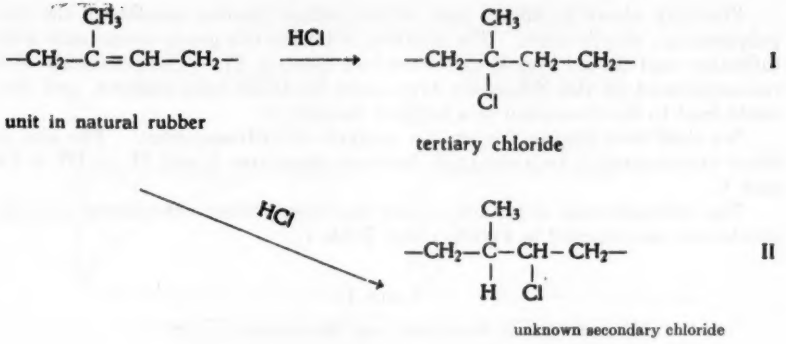
HYDROCHLORIDES DERIVED FROM NATURAL AND SYNTHETIC RUBBER

The isopentene unit in natural rubber adds HCl readily at very low temperatures in the solid state, in solution[2], or in latex[3]. Earlier suggestions[4] that the reaction product is a mixture of tertiary (I) and secondary (II) chlorides, have already been refuted[2], and we found no indication of a deviation from Markownikoff's rule.

The hydrochloride of natural rubber approaches closely the composition $(C_5H_9Cl)_n$, whereas the isomer from polyisoprene adds HCl incompletely. This may be due either to a loss of double bonds in the polymer as a result of cyclization, or to a lack of reactivity of vinyl groups in the polyisoprene.

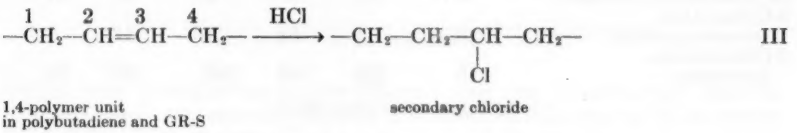
This ease of reaction of methylated double bonds is in marked contrast to the reactivity of double bonds present in polybutadiene, the olefinic part of

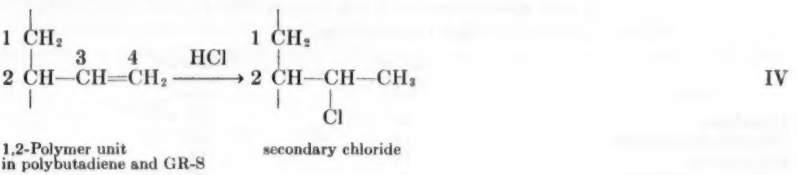
* Reprinted from the *Recueil des Travaux Chimiques des Pays-Bas*, Vol. 69, No. 5, pages 711–723, May 1950. This paper is Communication No. 104 of the Rubber Foundation, Delft, Holland.

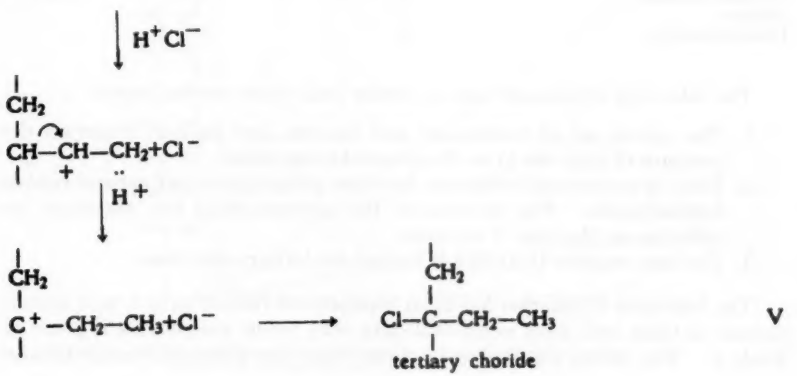


GR-S. We were interested in the reaction of these groups with HCl, first because the chlorides should be secondary, and secondly because double bonds of this type may be formed by rearrangement in some derivatives of natural rubber. In fact we found that HCl can be added to GR-S and Perbunan at elevated temperatures and pressures.

GR-S is known to contain about 80 per cent of the 1,4-polymer unit, which must lead with HCl to the secondary chloride III.







Probably about 15–20 per cent of the olefinic fraction consists of the 1,2-polymer, *i.e.*, vinylic units. The addition of HCl to this group occurs only with difficulty, and should lead to the secondary chloride IV. The possibility of a rearrangement of the Whitmore type must be taken into account, and this could lead to the formation of a tertiary chloride V.

We shall now discuss the kinetic analysis of hydrochlorides. The aim of these experiments is to distinguish between structures I and II or III + IV and V.

The hydrochloride of natural rubber has been studied extensively, and the results are summarized in Figure 1 and Table I.

TABLE I

REACTIVITY OF POLYMERS AND MONOMERS AT 100° C

a. Standard test conditions

Half time in hours

	Pure base at 100° C			4 vols. nitrobenzene + 1 vol. base at 100° C		
	Aniline	Pyridine	Piperidine	Aniline	Pyridine	Piperidine
Polymer						
Natural rubber—HCl	1	11	25	6	17	13
Polyisoprene—HCl	1.5	11	15	7	11	9
Model						
2-Chloro-2-methylbutane	0.17	40	30	4	34	15
3-Chloro-2,2,3-trimethylpentane	0.05	4	64	1.5	11	5
2-Chlorobutane (secondary)	10	250	340	200	400	26

b. Influence of some bases

(4 vols. nitrobenzene + 1 vol. base at 100° C)

Half time in hours

Base	Natural rubber HCl	2-Chloro-2 methyl-butane
Piperidine	13	15
N-methylpiperidine	15	43
Butylamine	10	13
Cyclohexylamine	12	17
Aniline	6	4
Dimethylaniline	31	53

The following conclusions can be drawn from these measurements.

1. The curves are all continuous and smooth, and indicate therefore the presence of only one type of carbon-chlorine bond.
2. There is no essential difference between polyisoprene and natural rubber hydrochloride. The structure of the polymer chain has, therefore, no influence on the rate of reaction.
3. The fast reaction in aniline is typical for tertiary chlorides.

The half-time of reaction has been interpolated from Figure 1, and a comparison of these and some additional data with model compounds is given in Table I. The values are similar to those found for 2-chloro-2-methylbutane

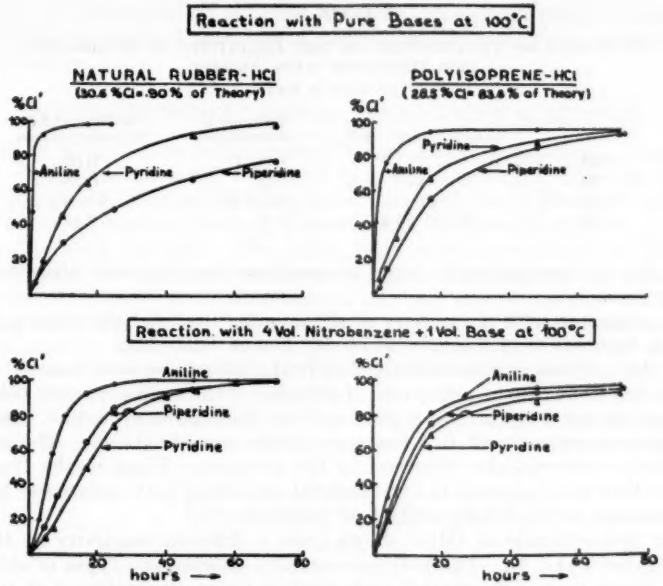


FIG. 1.—Reaction of hydrochlorides of natural rubber and polyisoprene with pure and diluted organic bases at 100° C.

and the order of magnitude is quite different from that of a secondary chloride. The macromolecular state has, therefore, no essential influence on the reactivity of the tertiary chlorine group.

Measurements with the hydrochloride of natural rubber in aniline were now extended to lower temperatures. The reactions do not deviate much from first

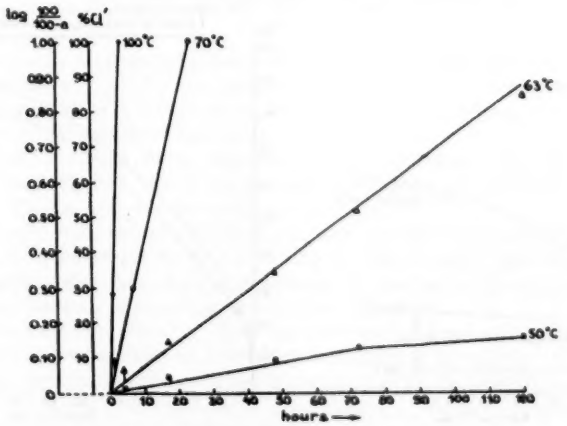


FIG. 2.—Influence of temperature on the reaction between rubber hydrochloride and aniline, logarithmic scale (a = % Cl').

TABLE II

INFLUENCE OF TEMPERATURE ON THE REACTIVITY OF RUBBER-HCl AND MONOMERS WITH ANILINE

Half time in hours

t° C	Natural rubber—HCl	2-Chloro-2-methylbutane	3-Chloro-2,2,3-trimethylpentane
100	1	0.17	0.05
70	3	2	0.59
63	39	(~ 4)	(~ 1)
50	Very slow	8	2.1

order, but an exceptionally large temperature function was observed (see Figure 2).

A comparison with the tertiary model revealed that the rate of the polymer reaction becomes much too slow at 60–50° C (see Table II).

As the polymer is incompletely dissolved under these conditions, the discrepancy must be due to a slow rate of diffusion of the aniline into the polymer. Attempts to use a mixture of a good solvent (benzene) and aniline, yielded a homogeneous polymer solution but poor kinetic reproducibility. The solvent is probably preferentially absorbed by the polymer. These results illustrate the fact that small changes in experimental conditions may apparently lead to complications in the kinetic analysis of polymers.

The hydrochloride of GR-S shows quite a different reactivity at 100° C (see Figures 3 and 4). The polymer contains at least two types of chlorine. About 20 per cent of the total is very reactive under all conditions at 100° C, and must be either tertiary or allylic. Part of this fraction is nonreactive in nitrobenzene-aniline at 50° C, and the assumption of a tertiary chloride group V is thus feasible. About 80 per cent of the chlorine is nonreactive with nitrobenzene-aniline at 100° C and moderately reactive with pure aniline at 100° C and with nitrobenzene-piperidine at 100° and 120° C. It therefore corresponds to the expected secondary chlorides III or IV. The shape of these curves intimates the existence of two secondary chlorides. The "very slow" fraction

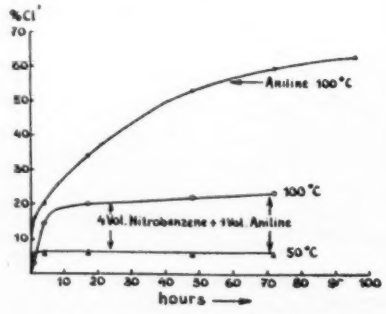


FIG. 3.—Kinetic analysis of GR-S hydrochloride with pure and diluted aniline.

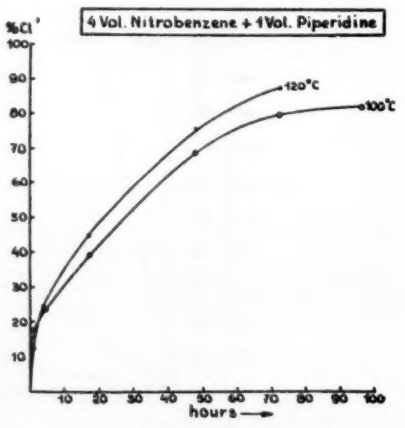


FIG. 4.—Kinetic analysis of GR-S hydrochloride with diluted piperidine.

might be a cyclic secondary chloride; however, the polymer was not completely dissolved, and Figure 4 does not at present therefore permit a more detailed interpretation.

HYDROBROMIDES DERIVED FROM NATURAL RUBBER

The addition of HBr to natural rubber occurs with great ease. Under peroxidic conditions one could expect at least some secondary bromide groups. As is well known, HBr added under these conditions of the Kharasch effect, in a radical chain reaction, leads to a reversion of Markownikoff's rule, and thus yields secondary bromides. The latter react with organic bases in hours at 50° C, whereas the tertiary bromides react at the same temperature in minutes[5]. A mixture of the two bromides should in any case lose all bromine on heating with bases at 50° C. The first bromide prepared with HBr gas from a rubber solution gave an unexpected kinetic picture (see Figure 5). About 20 per cent of the bromine was stable at 50° C in the presence of organic bases. This means probably that a polybromide or a dibromide containing about 20 per cent of the total bromine, presumably from the addition of bromine to the double bond, has been formed. The conjecture is supported by the fact that the HBr in

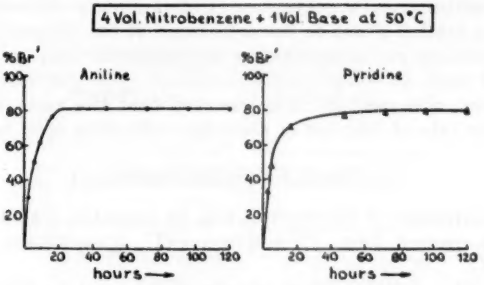


FIG. 5.—Kinetic analysis of rubber HBr. A product contaminated with rubber dibromide groups.

these experiments was prepared from decaline and bromine, and the presence of small quantities of bromine was not excluded. We have since prepared HBr by the combustion of bromine in a hydrogen stream, and have succeeded in obtaining pure rubber hydrobromides.

The hydrobromides differ chemically from the hydrochlorides but are physically very similar. Both are strongly crystalline and difficult to dissolve at 50° C. This in fact creates another source of error.

Heated only with the solvent-base mixture, reactivity indicates apparently two types of bromine groups. Preheating in the solvent alone above 50° C and then adding the base makes it possible to prepare a strongly swollen gel in which the reaction proceeds smoothly (see Figure 6).

We have shown previously[6] that the mixture aniline-nitrobenzene is suitable for a kinetic separation of secondary and tertiary bromides. Taking into account the physical factors outlined above, it should be possible to prove the presence of a secondary bromide with this reagent. We have prepared numerous hydrobromides from purified natural rubber, as well as from gutta-percha. Peroxides or antioxidants were added and approximately the theoretical amount

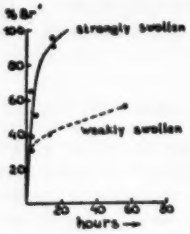


FIG. 6.—Influence of incomplete swelling with 4 volumes nitrobenzene + 1 volume aniline on the reactivity of rubber HBr at 50° C.

of HBr (53.6 per cent Br) was added to the polymer by bubbling HBr gas through the solution. The kinetic analysis of these polymers is summarized in Figure 7. None of the curves is indicative of a large fraction of secondary bromide. It must, therefore, be concluded that the Kharasch effect is difficult to realize in polymers with nonterminal double bonds. This has already been stated for low-molecular olefins by previous workers[7], unless extreme dilution is employed[8]. Up to this time we have failed to discover the corresponding experimental conditions with polymers. Unfortunately we had no secondary bromide with a methyl group in the α-position at our disposal. According to Tuot[9] these bromides are more reactive in hydrolysis than ordinary secondary bromides, and such an effect might invalidate our test method. We have stated[1], however, that we have not observed that the methyl group has any influence on the rate of reaction of secondary chlorides with bases.

POLYMERS OF CHLOROPRENE

The polymerization of chloroprene can, in principle, lead to three types of polymer units derived from 1,4-addition (VI), 3,4-addition (VII) and 1,2-addition (VIII).

Structures VI and VII are both vinylic, and cannot be distinguished kinetically. It has been proved by infrared analysis[10] that structure VII hardly

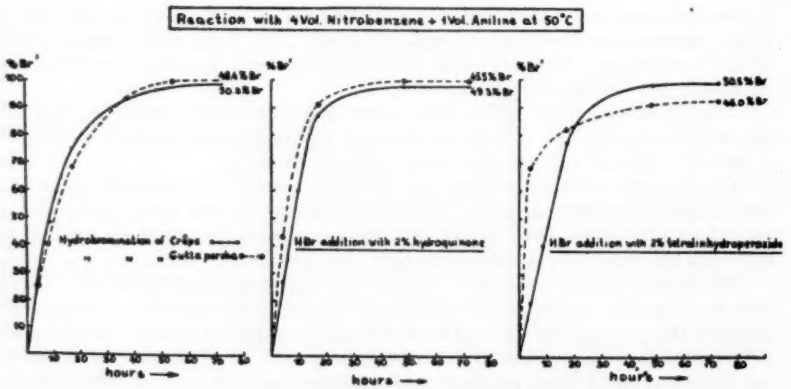
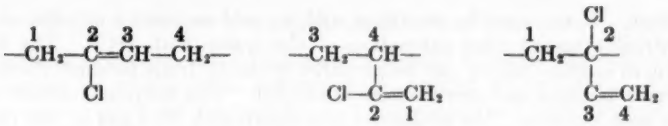

Reaction with 4 Vol. Nitrobenzene + 1 Vol. Aniline at 50°C
% Br
Hydrobromination of Crêpe
Gutta percha
HBr addition with 2% hydroquinone
HBr addition with 2% tetralinhydroperoxide
hours

FIG. 7.—Kinetic analysis of polymeric hydrobromides.



VI VII VIII

occurs. Structure VIII, on the other hand, is allylic and should reveal its presence by its reactivity.

We have analyzed two trade products after extraction with water and acetone. Neoprene GNA with 36.6 per cent Cl and Neoprene FR a freeze-resistant copolymer, presumably with isoprene and with a chlorine content of 30.4 per cent. Both polymers contain a proportion (about 5 per cent) of the total chlorine which reacts rapidly with aniline and piperidine (see Figure 8).

It can be concluded from Figure 8 that about 95 per cent of the chlorine in Neoprene has the expected stability of a vinyl chloride; whereas 5 per cent represents very reactive, presumably allylic, chloride groups. As all polymers known to us containing chlorine groups react more or less completely with piperidine dissolved in nitrobenzene on prolonged heating at 100° C, the observed nonreactivity is typical of Neoprene. This test is used in this laboratory as a routine method for the identification of Neoprene in finished goods.

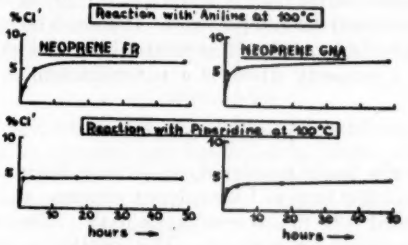


FIG. 8.—Reactivity of Neoprene with bases.

The discovery of a small quantity of allylic chloride suggests the interpretation of a phenomenon known as scorching to the rubber technologist. Zinc oxide reacts instantaneously with the allyl chloride groups in Neoprene. Mixing on the mill thus leads to the formation of zinc chloride. The latter compound is a strong catalyst for the polar polymerization of Neoprene, and therefore produces scorching. Magnesium oxide, on the other hand, also reacts with the allyl chloride groups in Neoprene, but the resulting magnesium chloride has no catalytic effect on the polymerization of Neoprene. Consequently the addition of magnesium oxide to Neoprene prevents the undesirable action of zinc oxide, which for other reasons is an essential ingredient of vulcanization mixtures.

EXPERIMENTAL PART

PREPARATION OF POLYMERS

Polyolefins with a methyl group on the double bond can be hydrochlorinated by bubbling HCl gas through a benzene solution of the polymer[3], precipitating the polymer with alcohol, and vacuum-drying the fine powder. Insoluble polymers are finely cut and suspended in the solvent without essential change of

procedure. Latex must be stabilized with an acid-resistent emulsifier and can be hydrochlorinated after saturation of the water with HCl[3]. The hydrochloride of natural rubber can be prepared from the trade product Pliofilm by solution in benzene and precipitation in alcohol. This polymer contains about 30 per cent chlorine. On additional treatment with HCl gas in the benzene solution, about 95 per cent of the theoretical number of double bonds, corresponding to a final chlorine content of 32 per cent, react.

Polymers of butadiene or GR-S can be hydrochlorinated by swelling 2 grams in 30 cc. of a mixture dioxane-toluene and saturating with HCl at $-10°$ C. Heating in a sealed Carius tube for about 24 hours at 70° C or about 10 hours at 100° C leads to a chlorine content of 60–80 per cent of the theoretically possible maximum. (In the case of GR-S, about 19–22 per cent chlorine.) The polymer is insoluble and can be purified by repeated swelling in benzene and precipitation in alcohol.

Hydrobromides of the former group of olefins can be prepared by identical methods. Hydrobromides of GR-S will be discussed in subsequent papers. It may be mentioned here that not more than 80 per cent of the double bonds react, but this reaction occurs readily at 50° C.

PROPERTIES OF POLYMERS

A detailed discussion of polymer structure will be given elsewhere[11], swelling and solubility have already been reported[12]. It should be emphasized that the hydrochlorides and hydrobromides of natural rubber and gutta-percha crystallize from solution, a property which is a potential source of error in kinetic measurements.

KINETIC ANALYSIS

100–400 mg. of the finely powdered, or at least finely cut, polymer is immersed in 5–10 cc. of the base or base-solvent mixture, and heated for the required time in a sealed tube in a thermostatic bath. The chlorine ion concentration is then determined by titration. The reaction as well as the titration are influenced by the degree of swelling of the polymer and the following precautions have to be taken.

We have in principle to deal with two cases.

(1) The halogen ion concentration under a given experimental condition is high and increases smoothly with time. In this case the degree of swelling is of minor importance, as the reaction is obviously not controlled by diffusion.

(2) The reaction proceeds slowly or comes to a sudden stop. To make sure that this is really due to the slow reactivity of a group and not to incomplete diffusion of the base into the polymer, we have to perform additional experiments. Working with a solution of the base in a solvent, it is possible first to superheat the polymer in the solvent and to add the base to the gel with vigorous shaking. Working with the pure base, repeated shaking during the experiment should not influence the reaction rate unless it is diffusion-controlled. Preswelling or superheating for a short time are also helpful in the detection of errors induced by incomplete swelling. In general it will be possible to circumvent such difficulties either by the choice of a higher reaction temperature or by a slightly different analytical system.

TITRATION

Solutions of the reaction mixture can be readily titrated, after separation of the polymer by precipitation and repeating washing with alcohol. The alcoholic solution of Cl′ is then acidified with nitric acid and silver nitrate added. The dark colors (from heating with aniline) are removed with small quantities of charcoal and, after filtering, the purified solution is titrated with thiocyanate solution.

Insoluble polymers may retain the base, and this may lead to errors, particularly in the case of aniline. Aniline dissolves silver nitrate, and this complex does not readily decompose in the presence of nitric acid. An apparently high chlorine ion concentration is found, due to the loss of silver ion. This error can be eliminated by treating the polymer for 24 hours with dilute nitric acid before titrating.

Another limitation is a measurable loss of chlorine ions by heating for a prolonged time with some solvents (dioxane, nitrobenzene) or some bases (aniline, piperidine) at 100° C or 120° C. The accuracy of an analysis therefore diminishes if extended beyond these periods.

Accuracy of the method for a polymer with a chlorine content between 25–60 per cent Cl is about 0.5 per cent Cl. It can be improved by adapting the titration to optimum conditions, which are specific for each polymer. A comparison of total chlorine determination in rubber hydrochloride by (1) heating with aniline and (2) with the conventional Carius analysis reveals that the latter is only slightly superior. This is probably because the homogeneity of such rubber derivatives is not equal to that of volatile organic halides, which can be purified by distillation.

SUMMARY

A number of hydrochlorides of natural and synthetic rubbers and allied polymers have been prepared and subjected to kinetic analysis with organic bases. The hydrochlorides of natural rubber react at 100° C at a rate identical to that of low-molecular tertiary chlorides. At 50° C the reactivity of the polymer is, however, reduced by physical factors.

The hydrochloride of GR-S (a synthetic rubber made from butadiene and styrene) has been prepared for the first time by heating the swollen polymer with HCl under pressure. Kinetic analysis of this product revealed two fractions: the expected secondary chloride, and a small fraction of a very reactive (tertiary?) chloride.

After elimination of experimental difficulties, we succeeded in the preparation and kinetic identification of the pure tertiary hydrobromide of natural rubber. Attempts to prepare the secondary bromide under peroxide conditions failed.

Kinetic analysis of two types of Neoprene revealed the presence of a small quantity of allylic groups in the polymer, while 95 per cent of the chlorine in Neoprene has the expected stability of a vinyl chloride. This stability can be used for the identification of Neoprene.

ACKNOWLEDGMENT

We wish to thank Miss A. M. Bourdillon for technical assistance and the Rubber Foundation for permission to publish. One of the authors (G. S.) is greatly indebted to Professor V. J. Koningsberger (Director of the Botanical Laboratory at the University of Utrecht) and his staff for generous hospitality under the adverse conditions of the war years 1940–1943.

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SOME PHYSICAL CHEMICAL PROPERTIES OF SOLUTIONS OF CHLORINATED RUBBER *

MARCEL RIOU AND RENÉ PIBAROT

INTRODUCTION

The molecule of chlorinated rubber, like that of every substance of high molecular weight, can be examined from two points of view, its microstructure and its macrostructure[1]. The microstructure, which depends on the nature of the atoms making up the chain (chemical composition), their spatial arrangement within the molecule (architecture of the molecule and its sterochemistry), and their interaction with the atoms of neighboring chains, governs the character of the whole product (fiber, rubber, plastic, etc.) and its chemical properties. This microstructural aspect of the problem will not be considered here.

On the other hand, the macrostructure does not depend on the nature of the atoms which make up the polymer, or on the closely located bonds which unite them, but it does depend on the general form of the molecules (whether linear, branched, or reticular), on the length of the chains, and on the distribution curve. It also plays a considerable role in the physical and technological properties of the product[2]. This shows the importance of having as exact an understanding as possible of the macrostructure of a polymer.

From this point of view, the present work had two objectives: (1) a study of the relation: $\eta/c = f(c)$ for crude chlorinated rubber, and (2) the determination of the distribution curves of different crude products, and of the limiting viscosity-molecular weight relation for homogeneous fractions prepared from the crude products.

PRINCIPLE OF THE EXPERIMENTAL METHODS

FRACTIONATION

Any natural or synthetic macromolecular substance is always heterogeneous. Chlorinated rubber, which is ordinarily prepared from natural rubber, is no exception to this rule; in fact, it shows a multiple heterogeneity, first, in its chemical composition and, secondly, in the architecture of its molecule (resulting from its method of preparation), and in the length of chain. Fractionation is always based on one particular property of a substance, in most cases its solubility, and two molecules of differing solubility can be thus separated under the same operating conditions.

In the present work it was found that the chlorine contents of the various fractions are much the same; hence there is no great chemical heterogeneity, and it can be disregarded in a first approximation.

New methods for determining the distribution curve of molecular weights have recently been described[3]. The conventional method is sharp fractionation, by which it is possible to obtain considerable quantities of fractionated products sufficiently homogeneous to be satisfactory for any subsequent study

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 27, No. 10, pages 596–600, October 1950.

which may be desired, *e.g.*, of the physical or mechanical properties, and, in particular, for the determination of the viscosity-molecular weight relation.

The most widely used processes for the fractionation of high polymers which are based on solubility are: (1) precipitation by successive additions of a non-solvent of chlorinated rubber to a solution of the polymer at constant temperature, and (2) successive extractions of the polymer by solvent-nonsolvent mixtures with increasing concentrations of solvent.

It should be pointed out, however, that with neither of these two methods can the individual molecular species of a polymer be sharply separated[4]. The first method gives fairly precise results provided that certain precautions are taken, *e.g.*, the use of sufficiently dilute solutions, slow precipitation at constant temperature, and washing of the precipitated fractions to eliminate substances of low molecular weight.

DETERMINATION OF MOLECULAR SIZE

The determination of the molecular size of a substance of high molecular weight is not simple, and most of the methods which have been proposed, though satisfactory in a relative way, require the preliminary construction of a standardization curve. Since not all the molecules are identical, a mean molecular weight is obtained, the value of which depends on the mean value chosen (numerical mean, weighted mean, etc.)[5], and consequently on the method used (osmotic pressure, light diffusion, etc.). In the present work, only the viscosity and the osmotic pressure methods were employed.

The viscosity of a solution has no simple meaning, for it depends on a large number of factors, and its interpretation is very difficult. However, it is a property which can be measured easily, and it is of theoretical interest as well.

On the contrary, the mean numerical molecular weight can be determined reliably by the osmotic pressure method. It has been found that, in some cases, the independent kinetic units of the polymer in solution represent actual molecules of the substance[6]. In other cases, the number of aggregates are determined.

RAW MATERIALS USED AND THE PRODUCTS STUDIED. APPLICATION OF THE EXPERIMENTAL METHODS

Various samples of chlorinated rubber from different sources were examined, including two samples of Parlon from the Hercules Powder Company, samples of Caoutchouc chloré Péchiney from the Compagnie Alais, Froges et Camargue, and products prepared in the laboratory.

All these products contained 60–62 per cent of chlorine[7]. In general, stable solvents were used, which were easy to purify by simple distillation, and which dissolved the chlorinated rubber rapidly without need of heating. These included toluene, monochlorobenzene, chloroform, and carbon tetrachloride. As a good precipitant of chlorinated rubber, methanol was chosen because of its solubility in the solvents mentioned and because of its volatility.

EXPERIMENTAL METHODS

The chlorinated rubber molecule is relatively fragile, and is very sensitive, when in solution, to the action of sunlight. All operations were, therefore, carried out with exclusion of sunlight.

DISSOLUTION

The quantity of chlorinated rubber to be dissolved was introduced into a calibrated flask; a few cubic centimeters of the solvent was added, and the mixture was agitated vigorously until the solvent was wholly imbibed. A further and larger addition of solvent then brought about complete solution after agitation for several hours. The solution obtained was filtered and diluted to the concentration desired.

FRACTIONATION

Thirty grams of chlorinated rubber was dissolved in 1000 cc. of toluene. When solution was complete, methanol was added slowly to the solution, with continuous mechanical agitation, until the solution became turbid. The solution was then cleared by heating at 22–23° C, following which the solution was allowed to cool very slowly to 20° C (the temperature of the thermostat). After standing several hours, the precipitated polymer collected in the form of a coacervate at the bottom of the receptacle. The clear supernatant liquid was decanted, and the fraction thus obtained was washed, first with a solvent-precipitant mixture composed of the same proportions of toluene and methanol as in the solution; then was washed with methanol. The product was next dried in a vacuum oven at 50° C and weighed.

In this way a certain number of fractions was obtained from each fractionation, and these were in some cases refractionated. A known quantity of each fraction was redissolved in a suitable solvent so as to obtain a solution of exactly 2 per cent concentration, which was then diluted to the concentrations desired.

After complete drying, the first fractions formed in most cases small quantities of gel. This phenomenon had already been found to be true of natural rubber[8] and of Neoprene[9].

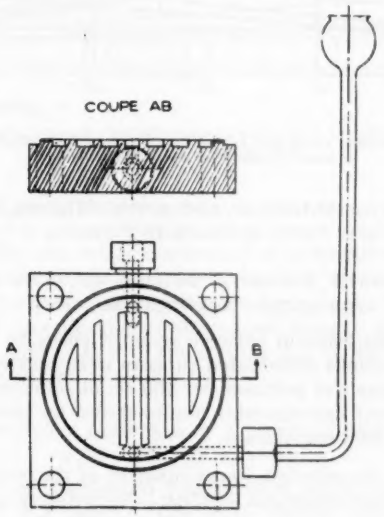

FIG. 1.—Differential osmometer.

OSMOTIC PRESSURE

The numerical molecular weights of different fractions were determined by the static method by means of osmometers which were essentially of the Duclaux type[10] and Fuoss type[11].

The osmometer of the Fuoss type is represented schematically in Figure 1.

The membranes were prepared from a solution of collodion, both by casting and by pouring on a glass plate.

For each sample, determinations were made in duplicate and at six concentrations. In most cases monochlorobenzene was used as the solvent.

From the results, curves were constructed as shown in Figure 2, with π/c as a function of $f(c)$.

LIMITING VISCOSITY

The viscosities of the crude products were measured in toluene and the viscosities of the fractions in monochlorobenzene, by means of a viscometer of the Beaumé Vigneron type[12]. The temperature was 20°. The measurements

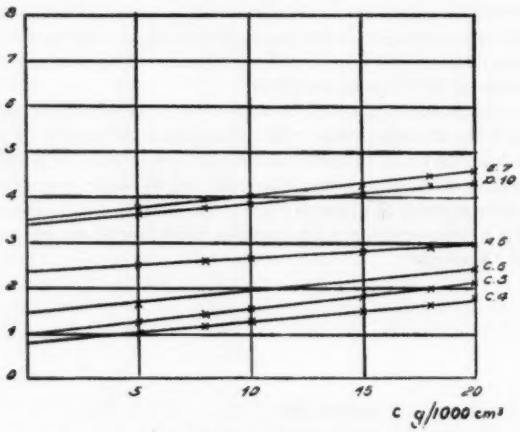

FIG. 2.—Relation: $\pi/c = f(c)$, for different fractions of chlorinated rubber in monochlorobenzene as solvent at 30°C.

were made at various concentrations, and curves of the results were constructed to show the relation: $\eta/c = f(c)$, as shown in Figure 3.

THE SPECIFIC VISCOSITY/LIMITING VISCOSITY RATIO FOR UNFRACTIONATED PRODUCTS

Curves showing the relation between reduced viscosity and the concentration of solutions of various chlorinated rubbers were constructed for the range 0.25 to 3 per cent (grams of polymer per 100 cc. of solution).

The most important experimental results shown by the curves in Figure 3 lead to the following two conclusions.

(1) The reduced viscosity is a linear function of the concentration, at least within the range of concentrations studied. Accordingly one may write:

$$\eta/c = [\eta] + Kc \qquad (1)$$

(2) All the straight lines thus obtained converge at the same point on the coordinates, *viz.*, at $\eta/c = 1$, and $c = -2.95$, on the particular reference system used. This group of straight lines is, consequently represented by the equation:

$$\frac{\eta_{sp}}{c} = [\eta] + \frac{\eta - 1c}{2.95} \tag{2}$$

Theoretical equations which have been proposed are generally of the form:

$$\frac{\eta_{sp}}{c} = [\eta] + K'[\eta]^2 c \tag{3}$$

The straight lines of a group do not pass through a single point, but are tangent to an enveloping curve.

In the present case, the range of limiting viscosities studied is relatively small, and the low viscosity values (0.1 to 0.6) are, therefore, not very precise.

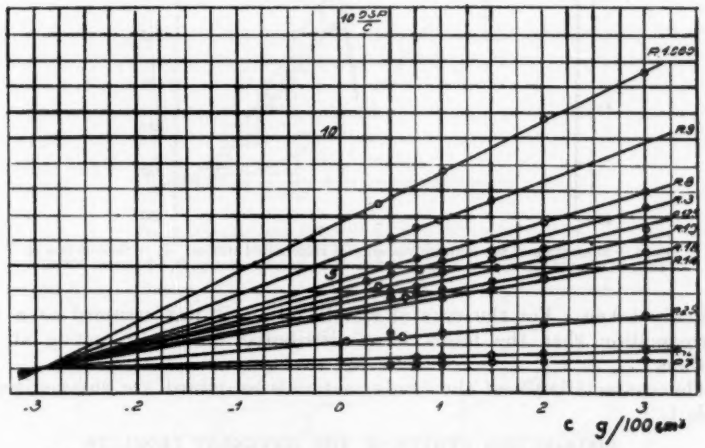

FIG. 3.—Relation: reduced viscosity-concentration (grams per 100 cc. of solution) with toluene as solvent and at 20° C.

It is probable that if products having a much wider range of limiting viscosities had been tested, such a group of straight lines would not have been obtained[13].

In spite of all this, the relation obtained is sufficiently precise to make it possible to characterize any product by its limiting viscosity simply by measuring its viscosity at a given concentration. A graph can then be constructed, for the range under investigation, which shows directly the limiting viscosity as a function of the time of flow of the solvent and of the solution in the same Beaumé-Vigneron viscometer (see Figure 4).

DISTRIBUTION CURVES AND A PHYSICAL–CHEMICAL STUDY OF THE FRACTIONS

Various samples of chlorinated rubber were fractionated by the method described earlier in this paper. The total weight recovered as individual fractions was, in general, of the order of 95 per cent of the amount of product

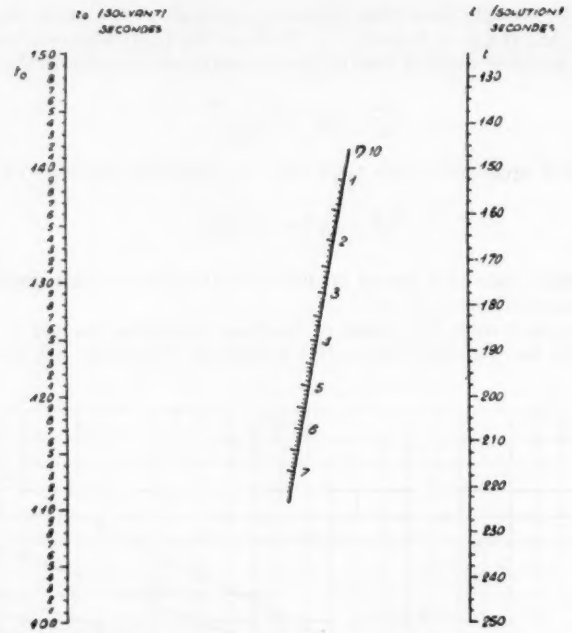

FIG. 4.—Monogram of the limiting viscosity of chlorinated rubber. t_0 = time of flow in seconds of pure solvent. t = time of flow of 1 per cent solution in toluene at 20° C.

originally taken. For the sake of simplification, it was assumed as a first approximation that the losses were distributed uniformly among all the fractions.

The characteristics of the crude materials examined are summarized in Table 1.

DISTRIBUTION CURVES OF THE DIFFERENT PRODUCTS

Figures 5 and 6 show the cumulative distribution curves. As judged by these curves, chlorinated rubbers are particularly heterogeneous in comparison with polymers such as polyvinyl chloride. This is, however, not so surprising when account is taken of the heterogenity and fragility of the material (natural rubber) from which they are derived, of chlorination itself, which involves severe treatment, and of the formation of solutions of the final product.

TABLE 1

LIMITING VISCOSITIES AND MEAN NUMERICAL MOLECULAR WEIGHTS OF THE VARIOUS CRUDE SAMPLES STUDIED
(Measurements at 20° C with monochlorobenzene as solvent)

Sample Identity	A Parlon 20-CPS	B Parlon 72-CPS	C Péchiney CC-6	D Péchiney CC-4	E Péchiney CC-2	F Laboratory preparation
$[\eta]$	0.21	0.45	0.8	0.47	0.32	1.10
$M \times 10^{-3}$	110	125	210	180	93	320
Chlorine (%)	62	62	61	60.5	62	60

THE LIMITING VISCOSITY–OSMOTIC MOLECULAR WEIGHT RELATION

Houwink[14] and Flory[15] have shown that the limiting viscosity-numerical molecular weight relation for homogeneous substances has the form:

$$[\eta] = KM^a$$

where K and a are two constants which depend on the nature of the polymer. Numerous investigators have determined these constants for different materials, including polyvinyl acetate, polymethyl methacrylate, polystyrene, polyisobutylene, natural rubber, and synthetic rubbers (GR-S, nitrile rubber, and Butyl rubber), etc.

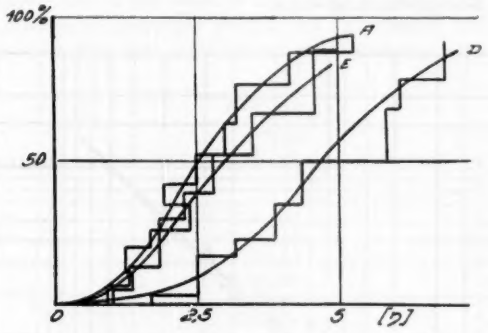

FIG. 5.—Distribution curves of different chlorinated rubbers. (A, D, E, as shown in Tables 1 and 2.)

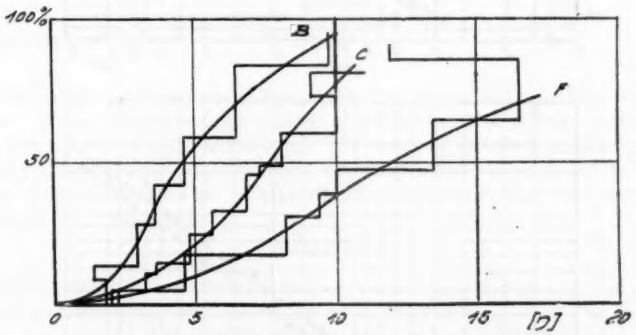

FIG. 6.—Distribution curves of different chlorinated rubbers. (B, C, and F, as shown in Tables 1 and 2.)

Two difficulties limit the value of the results; first, the precision of the measurements and, secondly, the relative homogeneity of the fractions.

The classic method consists of expressing the logarithm of $[\eta]$ as a function of the logarithm of M for each fraction. Equation (4) can then be written:

$$L[\eta] = LK + aLM \tag{5}$$

This is the equation of a straight line, the ordinate at the origin of which gives K and the slope a.

TABLE 2

VALUES OF K AND a FOR THE VARIOUS CHLORINATED RUBBERS STUDIED

Sample	A	B	C	D	E	F
$K \times 10^5$	0.9	1.5	4.7	4.7	5	5
a	0.87	0.89	0.75	0.75	0.82	0.75

Figure 7 shows some curves which conform to the relation (5). The results are for the samples shown in Table 2.

An examination of the data in Table 2 leads to the following conclusions.

(1) Relation (5) is confirmed, *i.e.*, the curves are actually straight lines within the limits of experimental error.

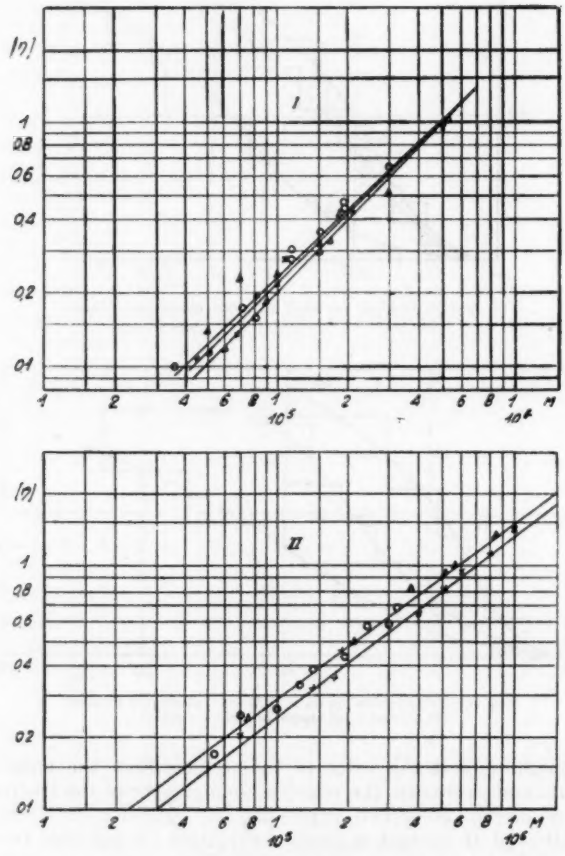

FIG. 7.—Relations limiting viscosity-numerical molecular weight, for various chlorinated rubbers in solution in monochlorobenzene

I △ A ○ B × C

II △ F ○ D × C

(2) The values of a are practically equal within the two groups A, B, and E, and F, D, and C, respectively.

(3) The K values are practically equal for samples A and B on the one hand, and for C, D, E, and F on the other.

(4) If the straight lines having the same slope are grouped on the same graph, as in Figure 7, it is found that the mean straight line which can be constructed corresponds to the values: $a = 0.73$ and $K = 5.7 \times 10^{-5}$, and $a = 0.85$ and $K = 2.4 \times 10^{-5}$, respectively.

Table 3 gives some values of K and of a for different products, as reported in the literature.

The K values are of the order of 10^{-4} for all the products. The values for chlorinated rubber are of the order of 10^{-5}, that is, decidedly lower. In other words, if the numerical molecular weight of a chlorinated rubber is normal, its limiting viscosity is very low, a fact to which Staudinger also has called attention[23].

TABLE 3

Product	Solvent	$K \times 10^{-4}$	a
Polyvinyl acetate[16]	Acetone	1.88	0.69
		1.76	0.68
Natural rubber[17]	Toluene	5.02	0.667
Polybutadiene[18]	Toluene	11.0	0.62
Buna-N	Toluene	4.9	0.64
	Acetone	5.0	0.64
	Benzene	1.3	0.55
Neoprene[19]	Toluene	5.0	0.615
		2.6	0.64
Polystyrene[20]	Toluene	3.7	0.62
	Methylethyl ketone	7.0	0.53
Cellulose acetobutyrate[21]	Acetone	1.37	0.83
	Acetic acid	1.46	0.83
Polyvinyl alcohol[22]	Water	2	0.78

Chlorination reduces, then, by about ten times the K value of natural rubber. The a values are close to those of cellulose acetobutyrate, but definitely higher than those of natural rubber. The exact physical-chemical significance of these constants is difficult to define with any degree of certainty at this time because of the difficulties which still exist in trying to explain the viscosity of a macromolecular solution[24].

SUMMARY

A study, from the viewpoint of macrostructure, of some of the physical-chemical properties of chlorinated rubber is described.

The cumulative distribution curves and determinations of the viscosity and osmotic pressures of dilute solutions make it possible to relate by simple laws the specific viscosity to the limiting viscosity, and the limiting viscosity to the osmotic molecular weight, and thereby to calculate the K and a coefficients by the relation of Huggins and Flory:

$$[\eta] = KM^a$$

In addition to their practical interest, such as the rapid determination of the limiting viscosity and of the molecular weight, the results have a theoretical significance which should not be underestimated, for they offer an approach to the problems involved in the interaction of a polymer and a solvent.

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A RAPID DETERMINATION OF THE AVERAGE MOLECULAR WEIGHT OF RUBBER IN HEVEA LATEX*

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Viscometric determinations of molecular weights of polymers in solution have found extensive applications. Despite the fact that there are many theoretical objections to this method, and that absolute determinations of molecular weights are possible only by comparing them with values that have been obtained in other ways, *e.g.*, osmometrically, by ultracentrifuge, etc., this method is nevertheless serviceable if one aims at obtaining relative data in large outline of polymers of various origins.

The basis of molecular weight determination by viscometric means is the Staudinger equation:

$$\frac{\eta_{sp}}{c} = KM \tag{1}$$

in which η_{sp} = the specific viscosity
c = concentration in grams per 100 cc. of solution
K = a constant characteristic of a given polymer-solvent system
M = molecular weight

In actual practice the molecular weight, determined by means of an absolute method (for instance osmometrically), is proportional to η_{sp}/c when extrapolated to infinite dilution:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = KM \tag{2}$$

in which $[\eta]$ = the intrinsic viscosity.

Houwink[1] and Flory[2] have shown that the general formula:

$$[\eta] = KM^a \tag{3}$$

is more satisfactory, a being a constant for any particular system.

If one wishes to carry out molecular-weight determinations of rubber in fresh latex, it is necessary to find a method whereby the rubber is dissolved as quickly as possible. The usual method, according to which the latex is first dried and the dried rubber is dissolved in a solvent, takes too long. For in such case one must first obtain a tiny piece of solid rubber either by pouring out and drying to a film, or by coagulating and drying the rubber. This takes several days, during which important changes in the rubber molecules can be produced under influences from outside (oxygen, light).

A system in which latex and a pure solvent can be mixed directly and continuously cannot be realized because the water in the latex will not mix with the customary rubber solvents.

* Reprinted from the *Recueil des Travaux Chimiques* des *Pays-Bas*, Vol. 69, No. 5, pages 753-758, May 1950. This paper is Communication No. 75 of the Indonesisch Instituut voor Rubberonderzoek.

The problem may be solved by using as a solvent the binary mixture of toluene and pyridine. This method, as far as we are aware, is not mentioned in the existing literature; only in an internal report of the I.G. Farbenindustrie[3] is there a casual mention of it.

In the INIRO Laboratory this method has been worked out further, with a view to carrying out viscosity determinations within an hour after having received the freshly tapped latex. Here the following method is applied: one cc. of 25 per cent Emulphor-O solution is added to 50 cc. of the latex, then water is added to make up to 100 cc., and 0.5 cc. of the diluted latex is pipetted into 100 cc. of the pyridine-toluene mixture (70 vol.-per cent of toluene and 30 vol.-per cent of pyridine). After thorough shaking, all the latex is found to be dissolved. It was found necessary to add a stabilizer (Emulphor-O), since otherwise coagulation occurs and the larger particles so formed do not dissolve readily.

The solvents used should previously be dried and redistilled. The concentration determination can now be made by vacuum evaporation of a certain quantity of the solution. In this connection, however, it was found difficult to obtain exact duplicates, so that it is more satisfactory to start with the dry rubber content (d.r.c.) of the fresh latex and calculate from this the rubber concentration in the solution.

The viscosity measurements were carried out with a viscometer of the Cannon-Fenske type at 35° ± 0.05° C.

In calculating the molecular weight, one may start with Formula (1), (2), or (3). The data found in the literature for the constants vary considerably. Thus, for instance, Gee[4] determined the following formula for rubber in benzene:

$$[\eta] = 1.6 \times 10^{-5} M^{0.96} \tag{4}$$

Carter, Scott and Magat[5] give for rubber in toluene:

$$[\eta] = 5.02 \times 10^{-4} M^{0.67} \tag{5}$$

Staudinger[6] gives:

$$\frac{\eta_{sp}}{c} = 1.4 \times 10^{-4} M \tag{6}$$

in which the concentration is expressed in base mole per liter. Calculated in grams per 100 cc., this becomes:

$$\frac{\eta_{sp}}{c} = 2.06 \times 10^{-5} M \tag{7}$$

Since the constants K and a also depend on the solvent, we have adopted for the time being the formula of Staudinger, since osmometrical measurements still must decide the value to be assigned to K and a for rubber in the pyridine-toluene mixture.

We may, however, compare the intrinsic viscosity of rubber in toluene and in a toluene-pyridine mixture. Masticated crepe is dissolved in these solvents, and viscosity measurements are carried out at several concentrations. In extrapolating to concentration zero we find the intrinsic viscosity of the different solutions (see graph).

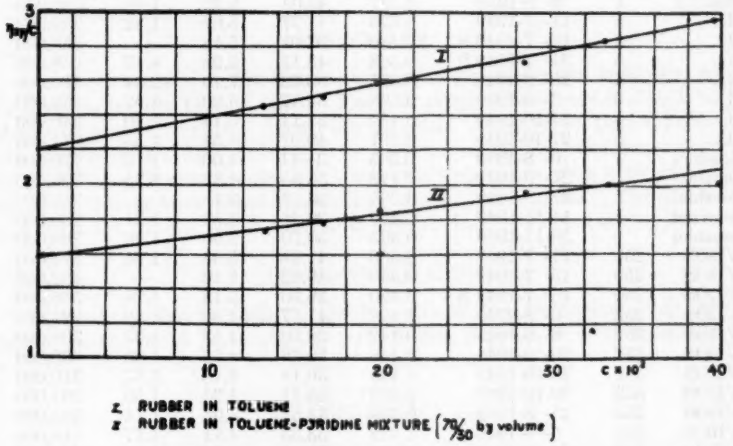
Using the Formula (7) of Staudinger, we can now calculate the K constant of the toluene-pyridine solution and find:

$$\frac{\eta_{sp}}{c} = 1.48 \times 10^{-5} M \tag{8}$$

or

$$M = \frac{\eta_{sp}}{c} \times \frac{1}{1.48} \times 10^5$$
$$M = \frac{\eta_{sp}}{c} \times 0.675 \times 10^5 \qquad (9)$$

The average molecular weights in this paper are calculated with this formula (Formula 9).



We must take into account that $\frac{\eta_{sp}}{c}$ is a function of the concentration.

In determining the molecular weight it was found, however, that extrapolation to infinite dilution is not essential, since the values found do not diverge greatly within the concentration range in which the work was done (see Table I).

TABLE I

Added quantity of latex per cc. after dilution 1:1 + Emulphor-0, 70 cc. toluene + 30 cc. pyridine. d.r.c. of fresh latex is 42.34.	η_{sp}	$\frac{\eta_{sp}}{c}$ c in g per 100 cc.	Molecular weight
1.00	0.927	4.38	296,000
0.50	0.430	4.06	274,000
0.25	0.211	4.03	272,000
0.10	0.088	3.11	278,000

This comparatively simple and quick method opens wide perspectives for a systematic investigation of clones. A number of samples of latex from trees of the garden of Tjiomas of the Experimental Station West Java were investigated the same morning the trees had been tapped.

Table II shows some results for different clones. The plasticities according to Hoekstra d_{18}^{70} of the whole latex rubber are also given.

TABLE II

Clone		Date of tapping	η_{sp}	d.r.c.	η_{sp}/c	d_{14}^{70}	Average molecular weight
Waringiana	I	4- 7-1949 S	0.316	25.60	4.94	1.76	334,000
Waringiana	I	7- 7-1949	0.555	41.14	5.40	—	363,000
Waringiana	I	13- 7-1949	0.564	39.79	5.68	2.12	384,000
Waringiana	I	14- 7-1949	0.460	32.43	5.66	1.89	382,000
Tjirandji	I	4- 7-1949 S	0.342	29.54	4.62	1.66	312,000
Tjirandji	I	13- 7-1949	0.559	39.64	5.64	2.00	382,000
Tjirandji	I	14- 7-1949 S	0.465	34.58	5.39	1.89	365,000
Tjirandji	I	6- 9-1949	0.680	39.88	6.82	2.06	460,000
Tjirandji	I	9- 9-1949	0.527	40.04	5.22	1.95	356,000
B.D.	5	11- 7-1949	0.628	44.77	5.62	1.82	380,000
B.D.	5	18- 7-1949 S	0.480	37.01	5.18	—	350,000
B.D.	5	21- 7-1949 S	0.568	43.13	5.28	1.87	358,000
B.D.	5	25- 8-1949	0.595	33.52	7.10	2.04	480,000
B.D.	5	3- 9-1949	0.508	39.17	5.20	1.92	352,000
B.D.	5	24-10-1949	0.425	33.11	5.14	1.80	346,000
B.D.	5	27-10-1949	0.567	40.97	5.54	1.84	374,000
Glenshiel	I	10- 8-1949	0.345	34.44	4.00	1.13	270,000
Glenshiel	I	21- 9-1949	0.442	36.65	4.82	1.74	326,000
Glenshiel	I	27- 9-1949	0.285	30.14	3.78	—	256,000
Glenshiel	I	14-11-1949	0.259	29.46	3.52	1.31	238,000
Glenshiel	I	26-11-1949	0.305	30.79	3.96	1.26	268,000
AVROS	256	11- 7-1949	0.580	41.84	5.54	1.94	374,000
AVROS	256	15- 7-1949	0.540	40.02	5.40	—	352,000
AVROS	256	16- 7-1949 S	0.470	36.66	5.13	1.78	346,000
AVROS	352	6- 8-1949	0.498	41.57	4.80	1.69	324,000
AVROS	352	8- 9-1949	0.442	38.80	4.53	1.83	306,000
AVROS	352	20- 9-1949	0.448	39.26	4.56	1.80	308,000
AVROS	352	26-10-1949	0.405	36.18	4.48	1.47	310,000
AVROS	352	29-10-1949	0.388	35.71	4.34	1.50	294,000
AVROS	255	25- 8-1949	0.438	34.53	5.08	1.78	343,000
AVROS	255	6- 9-1949	0.392	33.33	4.71	1.77	318,000
AVROS	255	24-10-1949	0.425	33.11	4.15	1.47	347,000
AVROS	385	30- 8-1949	0.620	40.52	6.12	2.39	414,000
AVROS	385	2- 9-1949	0.621	40.60	6.12	2.34	414,000

If not otherwise stated, the tapping system is normal (half bark circumference, every 2 days). S indicates that spiral tapping (full bark circumference, every 4 days) is applied.

It was also interesting to know whether the average molecular weight changes when preserved latex is stored.

Ammonia-preserved latex was stored in a brown bottle at room temperature (27.5° C). After some days, a viscosity determination of the latex solution in the pyridine-toluene mixture was regularly done.

Table III gives the results. The d.r.c. of the latex was 39.53.

TABLE III

Date	η_{sp}	η_{sp}/c	Average molecular weight
8-7-1949 Freshly tapped	0.487	4.92	332,000
11-7-1949	0.512	5.20	351,000
18-7-1949	0.520	5.26	356,000
23-7-1949	0.540	5.47	370,000
2-8-1949	0.495	5.01	338,000
13-8-1949	0.502	5.08	344,000

From these figures we may draw the following conclusions.

(1) There is some relation between the plasticity and the average molecular weight of rubber in latex. It is known, for example, that clone Glenshiel I gives a soft rubber and clone Avros 385 a hard one. The molecular weights are, respectively, about 300,000 and 400,000.
(2) Full spiral tapping tends to give on the whole a rubber with a somewhat higher plasticity and lower molecular weight.
(3) Fresh latex does not have a lower degree of polymerization than old preserved latex. During the first days of storing the average molecular weight tends to increase, but after a longer time it reaches its original value again.

SUMMARY

A method is described for determining viscometrically the molecular weight of rubber in freshly tapped latex. For this purpose the latex is dissolved in a toluene-pyridine mixture. From the intrinsic viscosity of this solution the molecular weight of the rubber can be determined by the Staudinger equation and a known viscosity constant. Molecular weights varying between 238,000 and 480,000 have been found, depending on the kind of clone. Rubber in fresh latex does not have a lower molecular weight than in old preserved latex.

ACKNOWLEDGMENT

Acknowledgment is made to the Director of the Indonesian Institute for Rubber Research for permission to publish this paper, and to the assistance of Soekarma in carrying out the viscosity determinations.

POSTSCRIPT

In preparing this paper, our attention was drawn to a publication of Henderson and Legge[7]. The authors carried out viscosity measurements of butadiene-styrene copolymers by dissolving the latex directly in a toluene-isopropanol mixture (80/20 by volume).

The work of the I.G. Farbenindustrie has been published briefly by Garten and Becker[8]. Pyridine-chlorobenzene mixtures are used for dissolving the Buna latex directly.

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STABILITY OF COMPOUNDED LATEX

K. W. HAYES

The thickening produced by zinc oxide in ammonia-preserved latex and the subsequent loss in stability of the latex are well known. Jordan[1] showed that the increase in viscosity in the presence of zinc oxide varied in accordance with the KOH number of the latex, and further showed that the addition of potassium hydroxide to the compound, equivalent in quantity to the KOH-number, reduced the amount of thickening. The mechanical stability was also shown to be related to the amount of thickening.

Wren[2] also showed the relationship between zinc oxide thickening and KOH number.

A surprising and rather obscure effect of zinc oxide thickening was described by Bächle[3] who showed that maximum thickening took place at a certain concentration of zinc oxide and then fell off as the amount of zinc oxide was increased. He drew curves of the viscosity and zinc oxide concentration, and found that distinct maxima existed in the region of 0.4 to 0.8 per cent zinc oxide, based on the rubber content of the compounds. He further stated that swelling tests indicated that the thickening was not a consequence of prevulcanization but depended on the concentration of zinc oxide. He showed also that the position of the maximum was practically independent of the amount of accelerator (Vulcacit P 774 and P extra N), although the zone of instability was enlarged most markedly on the right of the curve, where the zinc oxide content was greater. Increasing the sulfur content had a similar effect.

The above tests had included stabilizer and thickener. Without these being present, he found that thickening commenced much earlier and gave a much broader maximum, which spread into the region of higher zinc oxide content.

In view of the surprising effect of increasing the zinc oxide concentration, it seemed worth while to repeat some of the tests of Bächle.

The mixes in Table 1 were prepared. The dispersion of sulfur, zinc diethyldithiocarbamate, and zinc oxide were prepared by ball-milling, using the same 10 per cent solution of dispersing agent. The dispersing agent was an aromatic sulfonic acid type of high molecular weight.

The 10 per cent ammonia casein solution was prepared according to the following formula:

Casein	10
0.88 ammonia	2
Distilled water	88

As will be seen in Table 1, allowance was made for the increase of dispersing agent with increase of zinc oxide dispersion.

The viscosities of the 10 mixes were determined at regular intervals, as shown in Table 2, and represent the time required for 50 cc. to pass through an $\frac{1}{8}$-inch

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 26, No. 3, pages 223–232, October 1950.

TABLE 1

Ammonia content 0.45 per cent NH_3	60 per cent D.R.C. centrifuged latex	166.0 parts by wt.
	50 per cent Sulfur dispersion	4.0 parts by wt.
	25 per cent Z.D.C. dispersion	4.0 parts by wt.
	10 per cent Ammonia casein	2.5 parts by wt.
	50 per cent Zinc oxide dispersion	as below parts by wt.
	10 per cent Solution dispersing agent	as below parts by wt.

Mix number	50 per cent zinc oxide dispersion	10 per cent solution dispersin agent
1	0.2	9.9
2	0.4	9.8
3	0.6	9.7
4	0.8	9.6
5	1.2	9.4
6	1.4	9.3
7	4.0	8.0
8	8.0	6.0
9	10.0	5.0
10	20.0	—

diameter jet of ½ inch length. The viscosities were measured at a temperature of 20° C.

The samples were stored at a temperature of 18 to 20° C, and periodically were given a gentle stirring to ensure that settling-out of zinc oxide did not take place. In the case of Mix 10, the zinc oxide did settle out slightly. The volume effect of the zinc oxide on the viscosities can readily be seen from the viscosities at one day.

TABLE 2

Age of mixes (days)	Viscosity at 20° C (in seconds) Mix number									
	1	2	3	4	5	6	7	8	9	10
1	12.8	12.7	12.6	12.7	12.9	13.5	13.6	13.7	14.1	15.2
7	13.9	12.8	13.9	14.2	14.1	14.0	14.4	13.9	14.0	15.0
14	13.6	13.5	14.2	15.0	14.7	15.0	14.0	13.7	14.7	15.0
21	13.8	16.2	16.6	17.1	16.0	16.5	15.0	14.9	15.2	15.5
28	13.8	14.6	16.9	17.2	16.0	15.6	15.0	15.0	14.6	15.8
35	13.8	14.6	16.4	18.1	17.2	18.0	15.4	16.0	15.1	15.6
42	15.4	15.2	17.3	19.5	18.0	18.6	16.4	17.4	17.0	16.9
49	16.3	16.7	18.4	21.7	18.4	19.5	16.7	17.2	15.3	15.7
ZnO per 100 rubber	0.1	0.2	0.3	0.4	0.6	0.7	2.0	4.0	5.0	10.0

The viscosities at 1, 14, 28, 42 and 49 days are plotted in Figure 1, and the maxima are seen to occur at approximately 0.4 per cent zinc oxide.

To find the effect of increasing the ammonia concentration, Mixes 2, 3, 4 and 5 were repeated but with an ammonia content of 0.55 per cent NH_3 on the basic mix. The viscosities in Table 3 show that the maximum of the curve for viscosity and zinc oxide concentration were now out of this range. In actual fact, the maximum had been moved to the right towards the region of higher zinc oxide concentration.

Further mixes were prepared from the same base mix to find the effect of the addition of hydrochloric acid. The same base mix was used for all the viscosity experiments and, hence, the latex and other compounding ingredients were identical for all the various tests.

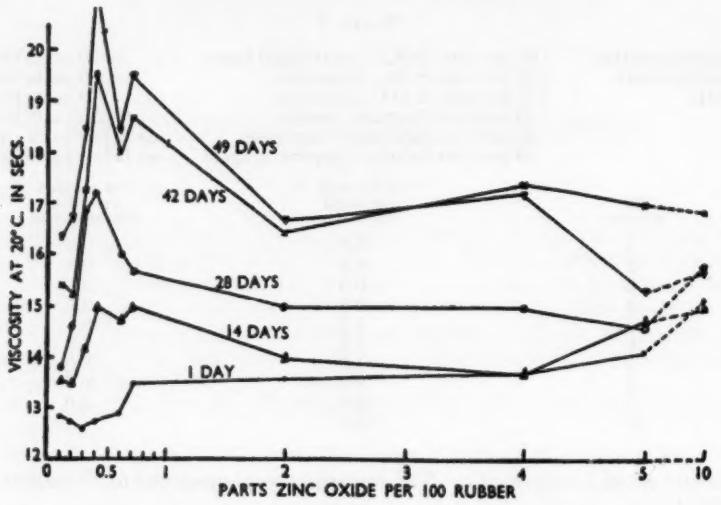

FIG. 1.

Mixes 2, 3, 4, 5 and 10 were repeated with 0.45 per cent NH_3, but with the addition of 1.0 cc. of 5 per cent hydrochloric acid solution to each mix. Table 4 shows that again the viscosities were still on the increase at Mix 5, but dropped again at Mix 10.

Observations on Mixes 1 to 10, with increasing zinc oxide content and 0.45 per cent NH_3, were interesting. On dipping a test-tube into each of the mixes and then into a coagulating bath of 10 per cent acetic acid solution, it was found that the latex films from Mixes 1 to 6 spread over the surface of the acid solution before coagulation was complete. With Mixes 7 to 10, the amount of latex spreading on the acid surface was noticeably reduced with increase of the zinc oxide content. This occurred at one day and throughout the period of test, irrespective of the heavier pick-ups with thicker samples.

The most obvious explanation appeared to be that the samples with higher zinc oxide content were either ionically less stable, or alternatively, some of the zinc oxide was becoming ionized in the acetic acid, the zinc ion concentration

TABLE 3

(0.55 per cent NH_3)

Age of mixes (days)	Viscosity at 20° C (in seconds) Mix number			
	2	3	4	5
1	12.8	12.9	12.7	12.9
7	12.9	13.3	14.4	14.2
14	13.4	13.8	14.9	15.3
21	14.8	15.4	17.0	17.5
28	14.9	15.4	19,0	20.2
35	15.2	16.6	20.7	22.2
42	14.6	16.9	21.5	24.8
ZnO per 100 rubber	0.2	0.3	0.4	0.6

increasing with the zinc oxide content and producing a rapid coagulating effect. The former possibility was judged as being unlikely in view of the viscosity values. The doubt was confirmed by carrying out gelation tests with a dispersion of sodium fluorsilicate. The main purpose of the gelation tests, however, was to gain some insight into the maximum thickening effect of the zinc oxide. The sodium fluorsilicate dispersion was prepared by ball-milling according to the following formula.

Sodium fluorsilicate	25
5 per cent solution dispersing agent	75

The dispersing agent was the same as used for the preparation of the dispersions of the vulcanizing ingredients.

The gelation tests were carried out as follows. To 70 grams of Mix 1 (0.45 per cent NH_3), after the 49 days' viscosity tests, 5 grams of the 25 per cent sodium fluorsilicate dispersion was added and the time determined for the formation of a thick paste. The mixture was stirred gently by hand by means of a glass rod. The pH at the thick paste stage was also determined by means of a glass-electrode pH meter.

TABLE 4

(0.45 per cent NH_3 and HCl added)

Age of mixes (days)	Viscosity at 20° C (in seconds) Mix number				
	2	3	4	5	10
1	13.2	13.2	13.4	13.1	15.2
7	13.4	14.0	14.0	15.0	15.6
14	13.7	15.0	16.4	17.7	15.1
21	14.8	17.6	20.0	24.8	16.0
28	14.8	17.0	20.0	27.6	16.6
35	14.8	18.3	23.0	35.6	17.3
42	16.0	19.2	25.6	46.0	16.9
49	16.2	19.3	25.0	55.0	17.8
ZnO per 100 rubber	0.2	0.3	0.4	0.6	10.0

Solid gels did not form for any of the Mixes 1 to 10, with the exception of Mix 4, which rapidly formed a solid gel. It would be more correct to say that sensitive pastes were formed by the other samples. Slightly increasing amounts of the mixes were used for this test with increase of the zinc oxide concentration, this being necessary to maintain a constant amount of rubber and other ingredients. Compared with the 70 grams of Mix 1, 71.6 grams of Mix 9 and 73.5 grams of Mix 10 were used. The results are shown in Table 5 (the samples were actually 51 days old at the time of test, *i.e.*, two days after the last viscosity determination). The pH values of all the samples were approximately 10.1 at the end of 49 days' storage period.

As a check on the results in Table 5, the tests were repeated two days later, that is, with the samples 53 days old. These results are shown in Table 6.

It will be seen that, apart from the slight increase of gelation pH, the results in Tables 5 and 6 are of the same order. During the tests at 53 days, the information in Table 7 was obtained. The results indicate that the samples of high zinc oxide content not only gelled at lower pH values but reached the lower values more quickly.

TABLE 5

(Mixes 51 days old)

Mix no.	Time to form sensitive paste (seconds)	pH at sensitive paste stage
1	160	8.90
2	137	9.06
3	136	8.82
4	75	9.19
5	80	9.34
6	77	9.35
7	103	8.80
8	146	7.47
9	175	7.25
10	188	7.10

To assess the degree of accuracy of the pH values, as the pH was found to be falling fairly rapidly during test, curves for the pH and time were drawn for each sample from the moment of the thick-paste stage. It was found that in 20 seconds a drop of approximately 0.1 pH unit occurred.

TABLE 6

(Mixes 53 days old)

Mix no.	Time to form sensitive paste (seconds)	pH at sensitive paste stage
1	151	8.97
2	132	9.13
3	137	9.00
4	70	9.30
5	64	9.37
6	64	9.33
7	102	9.00
8	139	8.18
9	184	7.90
10	200	7.56

The balance point on the galvanometer of the pH meter was attained in less than 5 seconds. The greatest inaccuracy was in deciding the thick-paste stage, although, after an initial thickening, detected by gently stirring with the glass rod, the thick-paste stage was rapidly attained.

Figure 2 shows the pH values at the thick-paste stage as a function of the zinc oxide concentration for the samples at 51 and 53 days.

TABLE 7

Mix no.	pH after 150 seconds	pH after 200 seconds
1	8.97	8.75
2	9.10	9.00
3	8.97	8.70
4	8.90	8.30
5	9.02	8.60
6	9.02	8.65
7	8.77	8.37
8	8.10	7.50
9	8.05	7.85
10	7.70	7.56

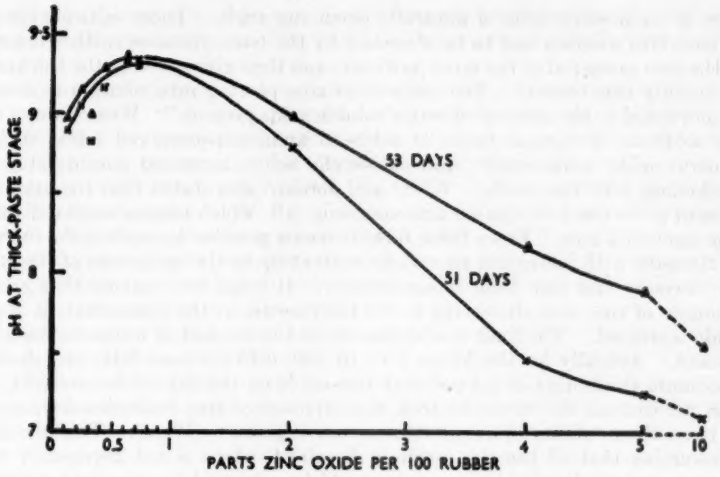

FIG. 2.

The tests described require some consideration to understand their significance. The sodium fluorsilicate dispersion was used in such an amount as to induce rapid gelation, the reason for this being that it has been found[4] that if sufficient sodium fluorsilicate is added to produce rapid gelation, the presence or absence of zinc oxide little affects the time or pH of gelation. Clearly this was a necessary step in view of the increasing concentration of zinc oxide in the mixes. The zinc oxide may be exerting some coagulating effect due to the formation of zinc ions, but even so, the time of gelation increased from Sample 4 to Sample 10.

Gelation tests were also carried out after 53 days on one each of the samples with added hydrochloric acid and higher ammonia content. The results are given in Table 8. Solid gels were formed in each case.

SIGNIFICANCE OF VISCOSITY AND GELATION EXPERIMENTS

The viscosity tests show that the thickening produced by zinc oxide decreases beyond a certain concentration. The critical concentration as shown by the maximum of the curves for viscosity and zinc oxide concentration has been shown to be affected by variation of the amount of acid and ammonia present. Bächle[3] also showed that variation in the amounts of other substances present, such as sulfur, accelerator, and stabilizer, could also slightly affect the position of the maximum.

Wren[2] stated the mechanism of zinc oxide thickening to be as follows: "Viscosity changes of zinc oxide-compounded latex are largely due to the pres-

TABLE 8

Mix number	Time to form gel (seconds)	pH at gelation
5 (plus HCl)	40	9.30
5 (0.55 per cent HN_3)	65	9.40

ence of ammonium salts of naturally occurring acids. These salts enable zinc to pass into solution and to be absorbed by the latex globules (with a lowering of the zeta potential of the latex particles) and thus giving rise to the thickening commonly experienced. The amount of zinc passing into solution is directly proportional to the amount of water soluble acids present." Wren showed that the addition of various types of acids to ammonia-preserved latex, such as mineral acids, amino-acids, and carboxylic acids, increased considerably the thickening with zinc oxide. Wren[2] and Jordan[1] also stated that the ammonia present gives rise to a soluble zinc-ammonia salt, which ionizes to give divalent zinc-ammonia ions. From these facts it seems possible to explain the increase of viscosity with increasing zinc oxide content up to the maximum of the curve for viscosity and zinc oxide concentration. It could be assumed that greater amounts of zinc were dissolving in the latex serum as the concentration of zinc oxide increased. The limit would depend on the amount of water-soluble acids present. Actually for the Mixes 1 to 10 with 0.45 per cent NH_3 and showing maximum thickening at 0.4 per cent zinc oxide on the dry rubber content, *i.e.*, 0.48 per cent on the serum content, that amount of zinc oxide dissolved would be twice the solubility of zinc in latex serum as given by Wren[2]. This of course, is assuming that all the zinc oxide is dissolved, which is not necessarily true. The amount of dissolved zinc oxide would be expected to remain at a certain concentration, depending on the latex, further additions beyond this amount remaining not ionized. The thickening would be expected to rise to a certain value of viscosity and then remain at this value with further additions of zinc oxide. As the experimental results have shown, the viscosity does not rise to some value and then remain constant.

The fact that the samples of high zinc oxide content gelled at lower pH values than the rest indicated that a protective film had been formed at the surface of the latex particles. The only difference in the mixes in Table 1 was in the amount of zinc oxide present.

OTHER EVIDENCE OF A MAXIMUM INSTABILITY ZONE DUE TO ZINC OXIDE

Lepetit[5] in discussing the heat sensitization of old ammoniated latex by zinc oxide, stated that "doses of 0.25 and 0.50 per cent of zinc oxide, on the dry rubber, do not cause the latex to become sensitive to heat at 50° C; however, at 70° C, the sensitivity begins to appear with 0.5 per cent. Sensitivity reaches a maximum with 1 per cent of zinc oxide and, in this case the mixture remains stable for two months at ordinary temperature. A larger quantity would have tended to decrease the sensitivity slightly, and mixtures remain stable for three months; this effect is due to dilution and to the presence of a greater quantity of dispersing agent which accompanies the zinc oxide". It will be noted, in the present thickening experiments described, the quantity of dispersing agent and dilution were kept constant. The mechanism operating in Lepetit's experiments to decrease the sensitivity slightly with amounts of zinc oxide greater than 1 per cent, is probably the same as in the present series of experiments and not due to dilution and quantity of dispersing agent.

SUGGESTED MECHANISM OF THE MAXIMUM THICKENING EFFECT

The formation of zinc ammonia ions and zinc ions, due to the presence of ammonia and certain water soluble acids in the latex, are accepted as two factors leading to instability. The mechanism is divided into two parts, firstly, a lowering of the zeta potential of the latex particles, due to adsorption of the

divalent zinc and zinc ammonia ions, and secondly, desolvation of the latex particles due to the formation of insoluble zinc soaps at the rubber-water interface.

Another factor, generally recognized as functioning in latex compounds containing zinc oxide, is usually included in the above mentioned processes of destabilization. It is the formation of water soluble zinc compounds of amino acids. The most simple amino acid, namely glycine, which is present in latex as a protein breakdown product, forms[6] a water soluble zinc compound, with zinc oxide, which decomposes at 65–70° C with zinc oxide as a decomposition product. The zinc is apparently unionized in this water soluble compound.

Assuming the formation of the water soluble zinc glycinate to take place in the latex, it is possible that such a salt could function as a stabilizer if adsorbed in sufficient quantity by the latex particles.

Any increase in stability due to adsorption of zinc amino-acid salts, assuming that to be the case, would clearly have to be sufficient to off-set the destabilizing effect of divalent zinc ions. Clearly also, the ratio of amino-acids to other water soluble acids which give zinc ion in solution, would be an important

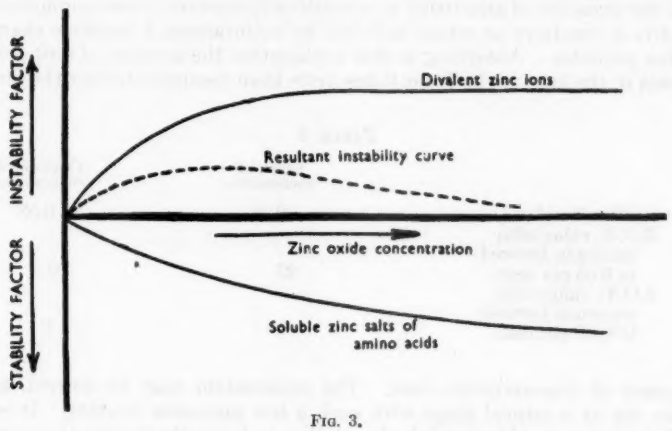

FIG. 3.

factor in determining the amount of zinc oxide thickening produced. According to Baker[7] experiments on ammonia preserved latex showed that the acids present are distributed as a large and markedly variable quantity of water-soluble acids in the water phase, in the form of ammonium salts, with nearly 1 per cent of long-chain acids at the surface of the rubber particle present as ammonia soaps, and over 1 per cent of miscellaneous acids dispersed in the rubber phase and occurring chiefiy as esters. He further showed that the water-soluble acids are partly degraded protein and hydrolysis products of esters of water-soluble acids. A fair proportion of soluble zinc salts of amino-acids could thus be formed in zinc oxide compounded latex.

The theory suggests that two opposing stability factors are at work when zinc oxide is added to ammonia-preserved latex. If these factors were equal and opposite, no thickening or loss in stability would result. In Figure 3 the two factors are shown diagrammatically. The *instability factor* due to divalent zinc ions has been indicated as rising to a definite value and then remaining con-

stant for further additions of zinc oxide. The *stability factor* has also been indicated to level-off but at a higher concentration of zinc oxide. The sum of the two curves gives a resultant with a maximum instability region. By reasoning that the upper curve would rise to a higher value and level off at a higher concentration of zinc oxide if the acid content of the latex was increased, it can be shown that the new resultant curve would have a maximum more to the right, in the region of higher zinc oxide content.

The theory is not contradictory to the accepted fact that the amount of zinc oxide going into solution in latex serum is directly proportional to the amount of acids present. It is, however, contradictory to the idea that the amount of zinc oxide going into solution is directly proportional to the amount of thickening produced. An interesting fact was given by Wren[2], who showed that there was no direct correlation between the amount of zinc oxide dissolved and the thickening produced.

The mechanism of zinc oxide thickening is certainly complex. Table 9 shows the results of Z.O.T. tests carried out on two different types of latex concentrate of almost identical KOH number.

The ammonia has a dual function. First, it should tend to cause destabilization in the presence of zinc oxide as a result of formation of zinc-ammonia ions. Secondly, it functions to retain stability by maintaining a negative charge on the latex particles. According to this explanation the increase of 0.04 per cent ammonia in the samples in Table 9 has more than compensated for the increase

TABLE 9

	Creamed concentrate	Centrifuged concentrate
KOH—Number	0.54	0.58
Z.O.T. value with ammonia lowered to 0.05 per cent	23	90
Z.O.T. value with ammonia lowered to 0.09 per cent	1	1

of amount of zinc-ammonia ions. The explanation may be correct, as the samples are at a critical stage with such a low ammonia content. It is suggested that the use of formaldehyde solution to lower the ammonia concentration in the Z.O.T. is probably a complicating factor.

To sum up, experimental evidence has been given to show that the stability of a latex compound increases with increase of zinc oxide concentration after passing through a minimum. Viscosity tests and gelation tests with sodium fluorsilicate provided the evidence.

It has been suggested that non-ionized water soluble-zinc salts are formed of certain amino-acids present in latex and that these salts function as stabilizers. The maximum thickening effect has been explained as the result of the opposing effects on stability of the ionized and non-ionized zinc salts in the latex compounds. Much more experimental work is needed to fully explain the mechanism of zinc oxide thickening.

SUMMARY

Thickening experiments with compounded latex are described showing the maximum thickening effect of zinc oxide when at a concentration of less than 1

per cent on the dry rubber content of a 60 per cent latex compound. Gelation tests with sodium fluorsilicate indicate that the curve relating the pH of gelation to the zinc oxide concentration is closely related to the curve showing the effect on the viscosity of the zinc oxide concentration. A theory is proposed to account for the maximum thickening effect.

ACKNOWLEDGMENT

The author wishes to thank Mr. H. Taylor for his valuable criticisms in preparing this paper.

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DETERMINATION OF COPPER IN RUBBER LATEX *

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INTRODUCTION

The difficulties in the determination of copper in rubber latex arise, not so much from the actual measurement of minute amounts of the copper ion, for which a number of well-proved methods exist, but from the fact that the copper is in association with many times its own weight of organic material from which it must be separated before the final assay of the metal can be carried out.

Probably the most widely used method for removing organic material is by dry ashing[1], but the danger of incomplete recovery of copper[2] has led to modifications of varying complexity, such as that proposed by O'Connor, Heinzelman, and Jefferson[3].

Difficulties in dry ashing are completely avoided by adopting a wet oxidation procedure, and this form of preliminary treatment has been accepted by two important testing authorities, the British Standards Institution[4], and the American Society for Testing Materials[5]. In general wet combustion methods are most reluctantly followed, as not only are they time-consuming to a degree, but they raise further difficulties by the introduction of large volumes of concentrations of unwanted salts to which still more separative processes must be applied.

More recently High[6] has reopened the question by carrying out a careful comparison of methods for the determination of copper in foodstuffs, and concludes that if the copper is extracted from the ash with a nitric acid-hydrochloric acid mixture, quantitative recovery of copper is obtained. The results quoted in High's work compare favorably with those obtained by the wet oxidation procedure.

It will be gathered that the picture presented by the literature is a fairly confused one, particularly as regards removal of organic matter and subsequent dissolution of the copper, and it was, therefore, decided to make a direct comparison of available methods and to examine the possibility of applying High's work to rubber latex.

EXPERIMENTAL WORK

OUTLINE OF METHODS

1. *Wet oxidation method.*—Five grams of the rubber sample is digested in a Kjeldahl flask with nitric acid and sulfuric acid until the organic matter has been destroyed. The copper is precipitated with hydrogen sulfide at an acid concentration of 25 grams sulfuric acid per 100 cc. and filtered with the sulfur, which is produced by adding a few drops of nitric acid with hydrogen sulfide still passing. The dried precipitate is ignited carefully in a porcelain crucible, and the residue moistened with nitric acid and evaporated. Copper in the am-

* Reprinted from the *Transactions of the Institution of The Rubber Industry*, Vol. 26, No. 3, pages 235–245, October 1950.

TABLE 1

COMPARISON OF COPPER CONTENT BY THREE METHODS

Method	Copper (per cent)	
Wet oxidation	0.00056	Duplicate determinations
	0.00052	
Dry ashing	0.00054	Replicate determinations
	0.00059	
	0.00057	
	0.00059	
Dry ashing with addition of magnesium nitrate	0.00059	

moniacal solution is then assayed by the usual colorimetric procedure with sodium diethyldithiocarbamate.

2. *Dry-ashing method.*—Five grams of sample is heated carefully in a sound porcelain crucible, first over a Bunsen flame, and finally in a muffle furnace at 800° C, until all organic matter and carbonaceous residue are removed. The ash is treated with a hydrochloric acid-nitric acid mixture, citric acid is added to suppress the precipitation of iron by ammonium hydroxide, and the determination is concluded with sodium diethyldithiocarbamate reagent.

3. *Dry ashing with magnesium nitrate.*—Five grams of the sample is heated in a porcelain crucible until the rubber is molten. Magnesium nitrate in the form of 25 per cent alcoholic solution is then added dropwise with further heating, and the ashing is concluded in a muffle furnace at 500° C. The final determination of copper is made as before.

A typical latex rubber was tested according to the procedures outlined, and the results are summarized in Table 1.

The results in Table 1 provide no evidence that losses of copper are sustained either by volatilization or failure to extract the copper from the ash, but the slightly higher results may be due to iron, which gives a slightly colored solution in the presence of citric acid.

The agreement between the figure obtained by all three methods was sufficiently close to encourage the comparison to be taken still further, and as the normal dry ashing procedure has the merit of simplicity compared with the magnesium nitrate modification, it was selected for a direct comparison with the wet oxidation method in further studies.

The consistency of the agreement was affirmed by determining the copper content, by both methods, of a number of natural rubber latex samples of different types. Results are presented in Table 2.

TABLE 2

COMPARISON OF COPPER CONTENT OF DIFFERENT LATICES BY TWO METHODS

Latex film	Copper (per cent)	
	West oxidation method	Dry ash method
60 per cent concentrate. Bulk shipment (A)	0.00054	0.00057
60 per cent concentrate. Bulk shipment (B)	0.00032	0.00038
60 per cent concentrate. Bulk shipment (C)	0.00044	0.00050
60 per cent concentrate. Bulk shipment (D)	0.00034	0.00039
60 per cent concentrate. Bulk shipment (E)	0.00044	0.00037
Electrodecanted	0.00049	0.00055
Type 4 (twice centrifuged)	0.00046	0.00046

From the results it appears permissible to assume that the dry ashing procedure is as reliable as the wet oxidation method except that a slightly higher figure is obtained presumably in the presence of iron.

Interference from iron.—A standard solution of ferrous iron was prepared from ferrous ammonium sulfate at a concentration equal to 0.0001 gram-iron per cc. The copper was removed from the solution by standing over chemically clean zinc. A similar stock solution of ferric iron was also prepared. In this case concentrated nitric acid was added immediately before use for the purpose of reoxidation.

To study the color intensity developed at appropriate stages by the addition of various reagents, the "copper equivalent" of the color produced for both ferrous and ferric solutions was measured. The results are given in Table 3.

Although exact matching of the colors in the two tubes is difficult on account of a slight difference in tint between the iron and the copper complexes, the above figures show that both ferrous and ferric iron are capable of exerting an appreciable interference with the final copper figure. In the case of ferric

TABLE 3

COPPER EQUIVALENTS OF IRON COMPLEXES

Reagents added to iron solution	Standard Copper Solution	Copper	Equivalent
	To match 0.2 mg. ferrous iron		
1. Critic acid + ammonia	0.15 cc.	0.0015 mg.	~1/130
2. As 1, + sodium diethyldithiocarbamate	additional 0.10 cc.	additional 0.0010 mg.	~1/200
Total	0.25 cc.	0.0025 mg.	~1/80
	To match 0.2 mg. ferric iron		
1. Citric acid + ammonia	0.2 ml.	0.0020 mg.	~1/100
2. As 1, + sodium diethyldithiocarbamate	additional 0.03 cc.	additional 0.0003 mg.	~1/700
Total	0.23 cc.	0.0023 mg.	~1/90

iron, the citrate complex has a preponderating influence on the color, whereas in the case of ferrous iron the effect of the diethyldithiocarbamate complex is comparatively more pronounced. The overall effect, however, is approximately equal, and the total difference between ferrous and ferric is well within experimental error.

The results show that, in the presence of citric acid, ammonia and sodium diethyldithiocarbamate, iron produces a color similar to, but much weaker than, that given by copper. The ratio of intensities at equal concentrations is approximately 1 to 100.

Comparison between the wet oxidation and dry ashing methods was extended over a wider range of copper contents by the addition of standard ammoniacal copper sulfate solution to weighted amounts of Type 4 latex. After thorough stirring, the latices were dried to films and their copper contents determined by both methods. Type 4 latex (Table 2) was chosen because of its low iron content.

The results are summarized in Table 4.

Within the limits of error imposed by visual methods (judged in the present instance to amount to about ±5 per cent), agreement between the two proced-

ures, as shown in Tables 1, 2, and 4, is reasonably close, particularly in the range of copper concentrations usually met in natural rubber latex (Table 2). For routine checks on latex supplies, therefore, and where the possible influence of iron on the result can be ignored, the simple dry-ashing procedure can be recommended.

Solution of the copper complex in carbon tetrachloride.—In some instances the concentration of iron is so high that its effect cannot be ignored. Furthermore, turbidity is sometimes caused by the presence of extraneous substances. To deal with cases of this nature, the following investigation was carried out, the essential feature being that the intensity of the copper complex is measured in a nonaqueous solvent.

Carbon tetrachloride was the solvent used for extraction of the complex, and the color absorption of the resulting solution was measured on the Spekker photoelectric absorptiometer to eliminate the personal error of matching solutions. The first experiments employed direct extraction of the complex after the reaction had taken place in the aqueous phase. A series of standard aqueous copper solutions was prepared containing different amounts of copper and,

TABLE 4

RECOVERY OF ADDED COPPER, COMPARISON OF TWO METHODS

Copper added, (per cent)	Copper found (per cent)			
	Wet oxidation method		Dry ashing method	
	Total	Recovered	Total	Recovered
0	0.00046	0	0.00046	0
0.00036	0.00079	0.00033	0.00074	0.00028
0.00072	0.00100	0.00054	0.00115	0.00069
0.00200	0.00230	0.00184	0.00250	0.00204
0.00300	—	—	0.00330	0.00284

in addition, citirc acid, ammonia in excess and sodium diethyldithiocarbamate. Each solution was extracted with several portions of carbon tetrachloride, and the final volume was made up to 10 or 25 cc. in a standard flask, according to the weight of copper expected.

It was found, however, that the carbon tetrachloride solutions were not always satisfactory for measurement, owing to two factors: turbidity due to water and occasional rapid fading, sometimes before extraction was complete.

Traces of water were removed in later experiments with anhydrous sodium sulfate (A.R. grade).

With regard to fading, it was found that this effect could be prevented by ensuring an excess of sodium diethyldithiocarbamate in the carbon tetrachloride layer, and the results from this modification are shown in Figure 1. Although, as before, extraction was made with either 10 or 25 cc. of carbon tetrachloride, the Spekker readings have been corrected to represent a common level of dilution of 10 cc.

It was found also that the zinc salt of diethyldithiocarbamic acid is more readily soluble in carbon tetrachloride than is the sodium salt, and also that zinc is more easily replaced by the copper. Advantage was, therefore, taken of these features to ensure a more uniform excess of reagent by working with the zinc salt in carbon tetrachloride. Results on a similar series of test solutions follow closely those obtained with sodium diethyldithiocarbamate, and are also shown in Figure 1. In each case the absorption measurements were made with

a mercury vapor source with Chance glass filter OB 1 (giving maximum transmission in the 430 mμ region) and 1-cm. cells. The drum was set to a value of 0.500 for carbon tetrachloride alone before readings were taken.

Optical density of dilute solutions.—In the previous experiments the range of copper content likely to be met in normal latex testing was covered. As each determination also involves an estimation of the copper content of the reagents used, *i.e.*, the blank determination, it was necessary to confirm that Beer's law was followed by solutions with low copper contents. The relationships between optical density and concentration are shown in Figure 2, from which it will be seen that with filter combination OB 2 and Wratten No. 50 the relationship is strictly linear, and with filter OB 1 it is approximately linear.

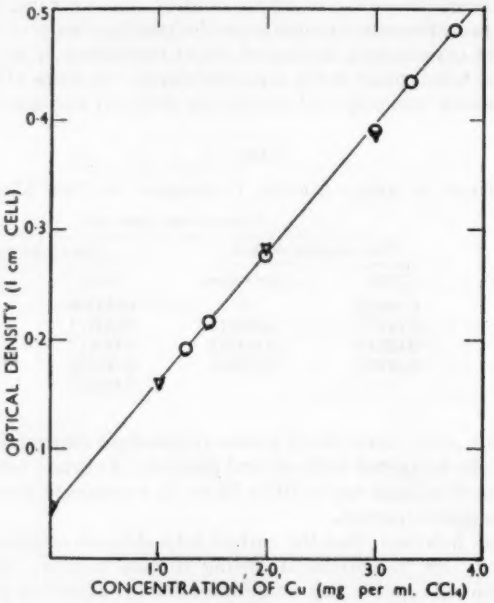

FIG. 1.

FIG. 1.—Optical density of solutions of copper diethyldithiocarbamate formed from: ○ sodium diethyldithiocarbamate. ▽ zinc diethyldithiocarbamate.

Interference from iron in carbon tetrachloride solution.—As interference from iron is in normal cases likely to be slight and of roughly the same order as that due to the copper in the reagents (normally the blank), it is necessary to assess the magnitude of these two factors separately. For this purpose use was made of the fact that copper forms a stable complex with cyanide and in the presence of cyanide therefore, the yellow color of the diethyldithiocarbamate compound might be expected to be suppressed. As the effect of potassium cyanide on the ferric diethyldithiocarbamate complex cannot be estimated directly, and the reagents used during the course of the extraction cannot be assumed to be copper-free, the effect can be estimated indirectly by a comparison of the color produced in the presence and absence of a copper-free ferric iron solution when

the same quantities of reagents are used. It was shown that this sequestering function of the cyanide operates in carbon tetrachloride solution, and it was, therefore, necessary to evaluate the color intensities at appropriate stages. A constant drop in optical density after treatment with potassium cyanide would indicate that the copper complex only is being decolorized. If the loss of color is greater in the presence of the iron complex, it too is being decolorized by the cyanide.

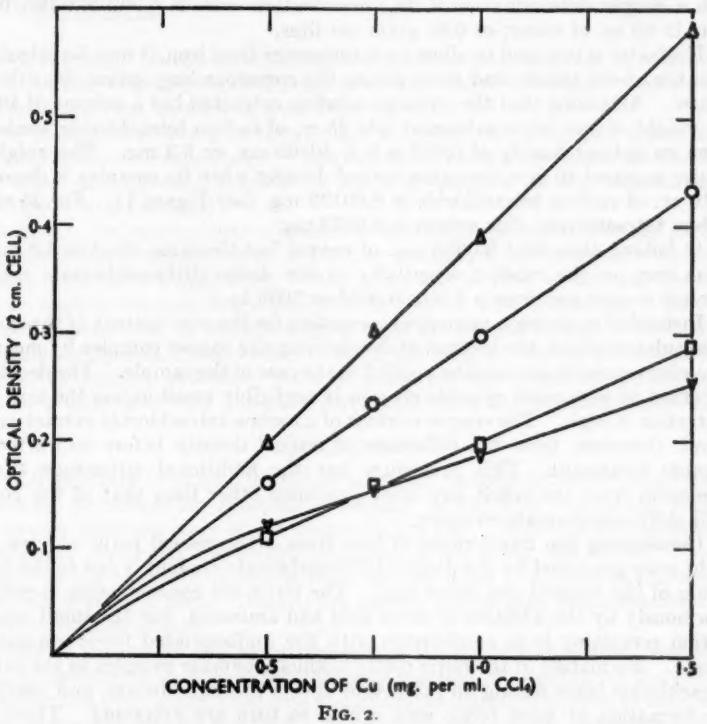

FIG. 2.

FIG. 2.—Optical density of solutions of copper diethyldithiocarbamate. Use of various filters. Δ OB2 + Wratten No. 50. ○ OB1. □ OV1 + Wratten No. 2. ▽ H556 (Hilger).

Three solutions were extracted: the first contained only the reagents used; the second contained in addition 0.005 gram of copper-free iron in solution, which was reoxidized before use; the third was made similarly with 0.025 gram of iron. In each case the volume was made up to 60 cc., 20 cc. of carbon tetrachloride solution of the reagent was used for the extraction, and 5 cc. was added to provide an excess of zinc diethyldithiocarbamate. The solutions were dehydrated and filtered, and their optical densities measured. Each solution was then treated with water and potassium cyanide for ten minutes, dehydrated, and filtered. The optical densities were again measured. The results obtained are summarized in Table 5.

From this table two conclusions may be drawn. First, the loss of optical density in the presence of iron shows that the iron complex is affected only

slightly by the presence of potassium cyanide, except when the iron solution is quite concentrated. Secondly, consideration of the difference between the optical densities of the three solutions before cyanide treatment shows that the absorption due to the iron is proportional to the concentration of iron salt in the water layer. This difference is 0.015 for an iron concentration of 0.005 gram in 60 cc. of water. Taking the limit of experimental error as corresponding to a Spekker absorptiometer measurement of 0.002, ferric iron will only interfere with a copper determination if its concentration exceeds $0.002 \times 0.005/0.015$ gram in 60 cc. of water, or 0.01 gram per liter.

If a factor is required to allow for interference from iron, it may be calculated from the above results and those giving the corresponding optical densities for copper. Assuming that the aqueous solution extracted has a volume of 40 cc., the weight of iron when extracted into 25 cc. of carbon tetrachloride needed to given an optical density of 0.015 is $5 \times 40/60$ mg. or 3.3 mg. The weight of copper required to give the same optical density when its complex is dissolved in 10 cc. of carbon tetrachloride is 0.00132 mg. (see Figure 1). For 25 cc. of carbon tetrachloride, this weight is 0.0033 mg.

It follows then that 0.0033 mg. of copper has the same effect as 3.3 mg. of ferric iron, so the relative sensitivity of the diethyldithiocarbamate reagent towards copper and iron is 3.3 to 0.0033 or 1000 to 1.

Instead of applying a numerical correction for the iron content of the sample as calculated above, the method of decolorizing the copper complex by means of potassium cyanide may also be applied in the case of the sample. The decolorizing effect of potassium cyanide on iron is negligibly small unless the iron concentration is high. The copper content of a carbon tetrachloride extract can be found, therefore, from the difference of optical density before and after the cyanide treatment. This procedure has the additional advantage that it eliminates from the result any color produced other than that of the copper diethyldithiocarbamate complex.

Considering the interference of iron from a theoretical point of view, the slight color produced by the diethyldithiocarbamate reagent is due to the interaction of the reagent and ferric ions. The ferric ion concentration is reduced enormously by the addition of citric acid and ammonia, but the small concentration remaining is in equilibrium with the undissociated ferric ammonium citrate. Formation of the ferric diethyldithiocarbamate complex in the carbon tetrachloride layer during an extraction upsets this equilibrium, and results in the formation of more ferric ions, which in turn are extracted. There are, accordingly two points of importance to be considered.

First, the iron continues to be extracted, even after all copper has been removed from the aqueous phase. This provides the possibility of allowing for interference from iron by performing a second identical extraction after removal of the copper, and finding the optical density of this second carbon tetra-

TABLE 5

EFFECT OF POTASSIUM CYANIDE ON THE FERRIC IRON COMPLEX

Weight of iron added to reagents	Optical density before KCN treatment	Optical density after KCN treatment	Difference
0	0.030	0.004	0.026
0.005 gram	0.045	0.018	0.027
0.025 gram	0.105	0.066	0.039

TABLE 6

EFFECT OF CONTINUED EXTRACTION OF IRON COMPLEX

	Optical density before KCN treatment	Optical density after KCN treatment
1st extraction	0.105	0.066
2nd extraction	0.102	0.099

chloride solution. When this operation was carried out, however, it was found that more iron complex was extracted after removal of the copper than during the first extraction, as may be seen from Table 6.

The method of allowing for interference from iron may introduce appreciable error, and it is not recommended. The results in Table 6 also show the decolorizing effect of potassium cyanide on the iron complex at this concentration (0.040 gram iron per liter).

Secondly, the consequence of continual extraction of iron is that the carbon tetrachloride layer collects more of the iron complex if left in contact with the aqueous layer for a longer time. This point was verified by leaving the iron solution used in the previous experiment in contact with a solution of zinc diethyldithiocarbamate in carbon tetrachloride for several hours. The carbon tetrachloride layer darkened visibly. When allowing for the iron present during a copper estimation, therefore, the time taken for the extraction should be as short as is consistent with complete layer separation and complete removal of copper.

CONCLUSIONS

Small amounts of copper in rubber latex can be determined by following a dry-ashing procedure for removal of organic matter and concluding with a colorimetric determination of the copper in the ash. Provided the ignition is not undubly prolonged, the ashing temperature can safely rise to 800° C, and recovery of the copper is complete from the ash when a mixture of nitric and hydrochloric acids is used. Results are slightly higher than those obtained by the wet oxidation process.

Assay of the copper can be carried out on the solution of the ash, either in aqueous medium or in carbon tetrachloride solution, depending on the extent of interference anticipated from iron and insoluble ingredients, such as clay, and on the degree of accuracy required. Visual color matching in aqueous solution is simpler and quicker, but insoluble material may give rise to considerable personal error. In aqueous solution, the copper equivalent of ferric iron is about 1/100, *i.e.*, the coloration is about 100 times more intense for copper than for iron.

For more accurate work, measurement of the color of a carbon tetrachloride solution of the copper diethyldithiocarbamate complex by means of a suitable colorimeter is recommended. The tendency of the complex to fade is overcome by replacing the sodium diethyldithiocarbamate by the zinc salt dissolved in carbon tetrachloride. In such a solution the copper equivalent of ferric iron is about 1/1000, but actual experimental conditions can vary this figure between wide limits. A more satisfactory procedure is, therefore, to measure the total color developed in carbon tetrachloride, and then bleach out the color due to copper with potassium cyanide. The residual (interfering) colors can thus be estimated, and the difference between the readings gives a direct measure of the concentrations of copper in the test solution.

ACKNOWLEDGMENT

The authors wish to thank the Technical Director of the Dunlop Rubber Company for permission to publish this paper.

APPENDIX

METHOD FOR THE DETERMINATION OF COPPER IN LATEX

Reagents:

1. Acid mixture	2 volumes concentrated hydrochloric acid. 1 volume concentrated nitric acid. 3 volumes distilled water.
2. Sodium diethyldithiocarbamate reagent	Moisten about 10 mg. gum tragacanth with about 1 cc. acetone and pour into 1 liter boiling water. When cool, dissolve in this solution 1 gram solid sodium diethyldithiocarbamate.
3. Standard copper solution	Weigh 0.1000 gram clean electrolytic copper into a small beaker and dissolve in dilute nitric acid. Wash down the beaker and cover glass, add 5 cc. concentrated sulfuric acid and heat to fuming. Cool, transfer to a 100-cc. volumetric flask, and dilute with distilled water to standard volume. Pipette 10 cc. of this solution into a liter flask and dilute to the mark with distilled water. This solution contains the equivalent of 0.01 mg. copper per cc.
4. Ammonium hydroxide (d. 0.890)	
5. Zinc diethyldithiocarbamate reagent	Dissolve 1 gram solid zinc diethyldithiocarbamate in 1 liter carbon tetrachloride.
6. Anhydrous sodium sulfate	
7. Citric acid, 10 per cent aqueous solution	
8. Potassium cyanide	

Procedure.—Weigh out accurately 3–5 grams of the latex film into a porcelain crucible of sound glaze and heat gently over a burner until all the rubber has been decomposed and a dry carbonaceous residue remains. Finally heat the crubible more strongly, in a muffle furnace if necessary, to a temperature not exceeding 800° C. Prolonged heating should be avoided, and should be terminated when the crucible and ash are completely free of carbon.

When the crucible is cool, note if the ash is considerable or colored by iron oxide, since in these cases it is desirable to conclude the determination by forming copper diethyldithiocarbamate in carbon tetrachloride solution (see later).

Add 10 cc. of the acid mixture (1) to the crucible, cover with a watch-glass and heat gently for 20 minutes. Wash the contents into a small beaker, add 10 cc. 10 per cent citric acid (7) followed by ammonium hydroxide (4) added dropwise until the solution is just alkaline to litmus, and then 2 cc. ammonium hydroxide (4) in excess.

In cases of normal ash or iron content as revealed by earlier inspection, transfer the ammoniacal solution to a Nessler column, add 10 cc. sodium diethyldithiocarbamate reagent (2) and make up 100 ml. with distilled water.

Prepare a blank solution from the same quantities of reagents and add 10 cc. sodium diethyldithiocarbamate reagent (2) to the diulted solution in the second Nessler cylinder. Run in the standard copper solution (3) from a burette until the intensity of the color produced matches that in the first cylinder, and take the burette reading (V cc.).

Then if the weight of the film taken for the test is W grams, the copper content is given by:

$$\frac{V \times 0.00001 \times 100 \text{ per cent}}{W}$$

If the total ash content of the latex is high or is strongly colored by iron oxide, add 10 cc. of the acid mixture (1) to the crucible, cover with a watch-glass, and heat gently for 20 minutes. Wash the contents into a small separating funnel, add 10 cc. 10 per cent citric acid (7), followed by ammonium hydroxide (4) added dropwise until the solution is just alkaline to litmus, and then 2 cc. ammonium hydroxide (4) in excess. Adjust the volume to about 40 cc. with distilled water and extract with three 5-cc. portions and one 3-cc. portion of zinc diethyldithiocarbamate reagent (5). Collect the carbon tetrachloride in a 25-cc. volumetric flask, and pipette into 5 cc. of the zinc diethyldithiocarbamate reagent (5). Finally shake the aqueous layer with a further 2-cc. reagent (5), and add to the bulk in the standard flask, adjusting the volume if necessary to 25 cc. with a few drops of the reagent (5).

To the solution in the flask add about 0.2 gram anhydrous sodium sulfate (6) and swirl the contents. If cloudiness persists after 10 minutes, add further small portions of annhydrous sodium sulfate (6), with swirling, until the solution becomes clear. After standing to allow the sodium sulfate to settle, decant a portion of the clear solution into the cell of a suitable colorimeter, and take the reading, using an appropriate filter combination.

Add 0.1 gram potassium cyanide (8) and 1 drop of distilled water to the solution in the cell, stir and stand for 10 minutes, remove the water with 0.2 gram anhydrous sodium sulfate (6) and filter. Return the clarified solution to the cell and measure the optical density using the same filter as before.

Correct the difference in readings by carrying out a blank determination on the reagents used, and from the corrected readings for the color density and the calibration curve for the instrument, obtain the concentration of copper in the test solution.

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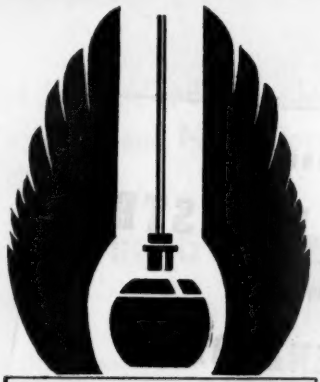

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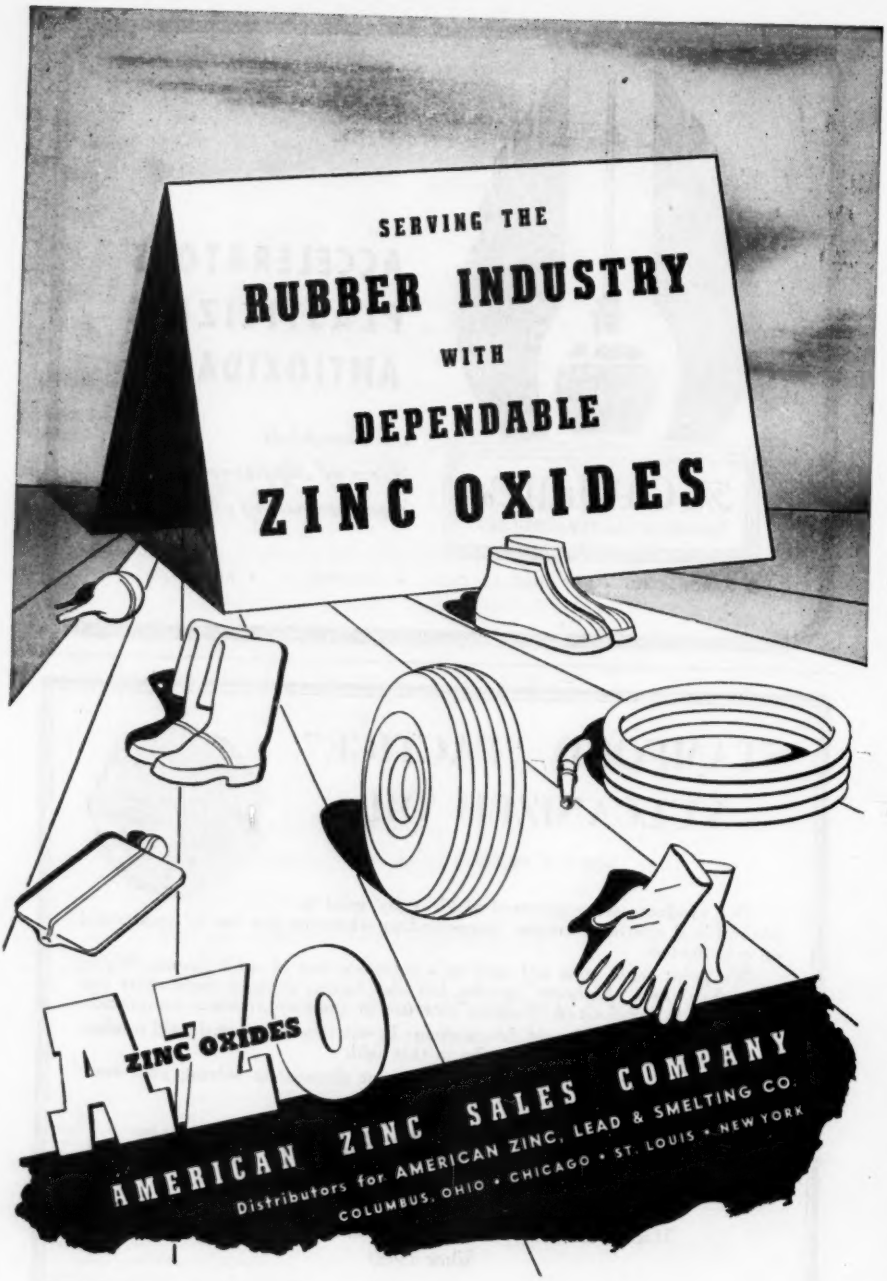
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The book has been divided into two parts. Section I concerns itself with the production of St. Joe commercially lead-free zinc oxides; it is a detailed and illustrated, step-by-step itinerary which begins underground in one of our zinc mines in upper New York State, and ends with the packing of the finished product in our Josephtown, Pennsylvania plant. Section II contains representative technical data on our various grades of black, red and green label zinc oxides, accompanied by photomicrographs and charts analyzing their particle size distribution characteristics. In addition, Section II includes a brief discussion of the role of zinc oxide in the major consuming industries.

Our reason for devoting twenty pages of this book to the production aspects of our zinc oxides will become apparent upon consideration of these facts: The trade term "Zinc Oxide" describes a series of materials that may be quite different from the material which is identified by the chemical symbol ZnO. Actually, ZnO is only a part of the materials thus described although its content is usually from 95.0 to 99.8% by weight. Other materials which may be a component part of commercial zinc oxides are, in some cases, beneficial and in others objectionable from the viewpoint of the consumer as well as the manufacturer.

Gentrally speaking, the characteristics possessed by the various zinc oxides now on the market were not developed by specifications set up by consumers, *but are the result of the various conditions surrounding the manufacture of the pigments.* A knowledge of zinc oxide production is thus an asset to consumers because different production methods result in pigments possessing different chemical or physical properties, and their applications have certain limitations which are important for consumers to recognize. This is the reason we have covered our production methods in considerable detail, and it is our belief that this will result not only in a better and wider utilization of commercially lead-free zinc oxides generally, but also in a greater appreciation of the high quality of St. Joe Zinc Oxides.

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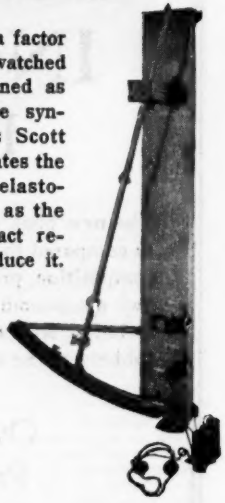

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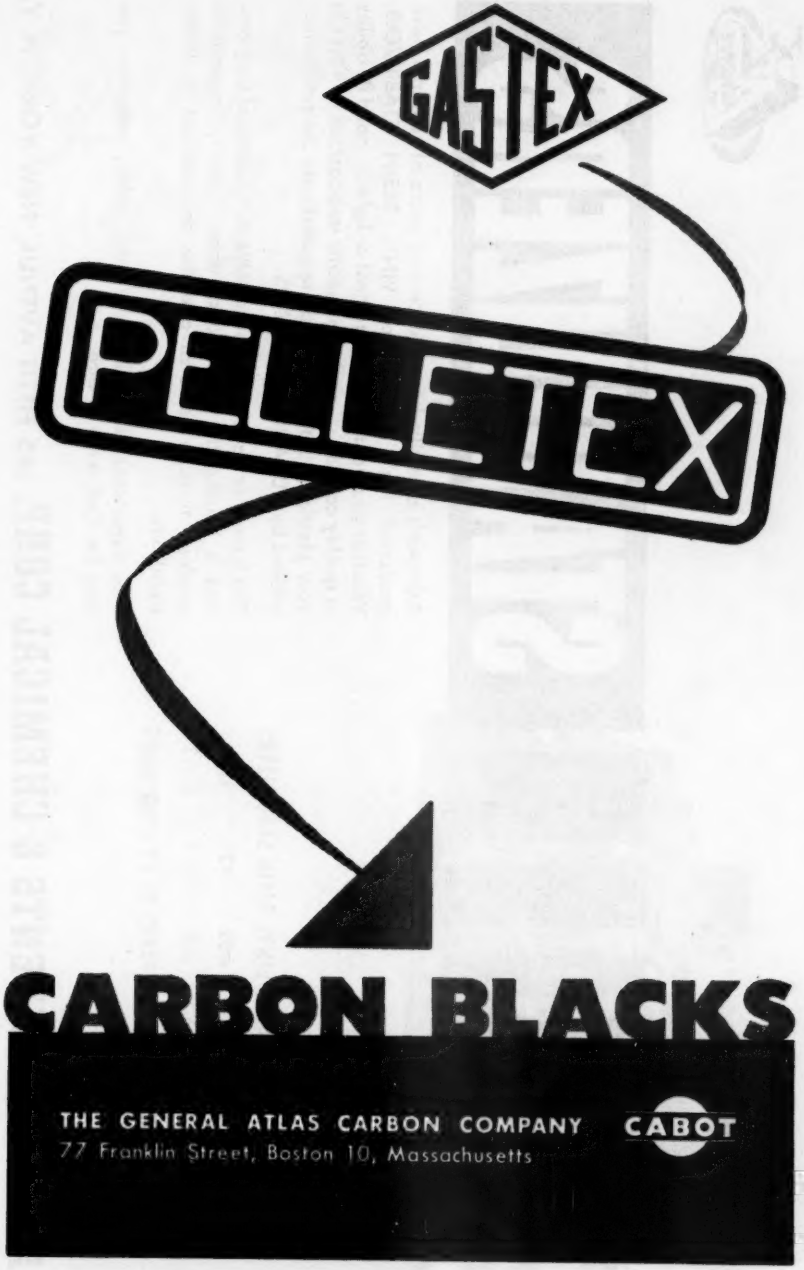
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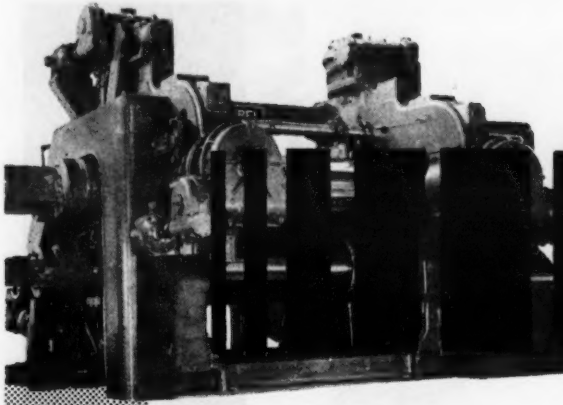

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IVATOR NEWS

A supplement to THE ACTIVATOR—the house organ issued by The New Jersey Zinc Company for over 15 years to aid the Rubber Industry in its use of Zinc Oxide.

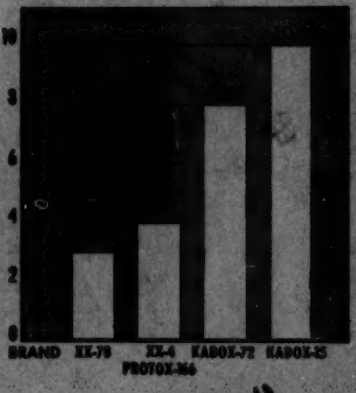
New Surface Area Values for HORSE HEAD ZINC OXIDES

THE surface areas of the various brands of Horse Head Zinc Oxides, when measured by the N_2 adsorption method*, are from 20%-65% larger than those derived from the electron-micrograph count method. The latter were previously reported in the March, 1949, issue of THE ACTIVATOR.

These findings stem from our extensive application of the N_2 adsorption method to a family of Zinc Oxides. Moreover, they represent an extension of the studies our Research Laboratories have been conducting on pigments for over thirty years.

Why the higher values? The N_2 adsorption method inherently measures the area of all particles; the count method estimates area through calculations based on length and width of a few hundred particles.

The new values for surface area are significant, as they accord more closely with the known processing and compounding properties of the individual Horse Head Zinc Oxides:



*Brunauer, Emmett and Teller, J. Amer. Chem. Soc. 60, 309 (1938).